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PREFACE

As the advances in science and technology continue, the border line between physics and chemistry becomes less distinct but increasingly interesting and important. Solid state physics, for example, suggests new approaches to many old problems. Removing mole fractions of contaminants of 10^{-8} which would otherwise spoil a transistor makes extravagant demands on methods of purification by zone refining. Adequately reporting advances in all fields is an ideal which at best can only be approached.

This year *Annual Review of Physical Chemistry* consists of twenty-one chapters in contrast to twenty-two last year. Seventeen chapters are devoted to the same fields reported in the last volume. Replacing "Kinetics of Polymerization," "Electrode Processes," "Combustion and Flames," "The Physical Chemistry of Proteins," and "Bond Energies" we have in this volume "Statistical Mechanics," "High Pressure Developments," "Optical Rotatory Power," and "Colloid Chemistry."

Again the authors of the various reviews have performed with distinction an outstanding service which will be generally appreciated. As in the past the reviews are the critical reports of experts in their fields of special competence. Any lack of balance will, we hope, be redressed in future volumes. The continued support by physical chemists, everywhere, is a source of genuine satisfaction. Mrs. Florene Dick served as Editorial Assistant and Dr. Donald Kupke has again compiled the subject index. The Editorial Committee deeply appreciate their services. The continued rapid advance in all fields of physical chemistry makes the preparation of *Annual Reviews* an exacting but very pleasant task.

C.J.C.	H.S.J.
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TOPICS AND AUTHORS

ANNUAL REVIEW OF PHYSICAL CHEMISTRY

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CONTENTS

THERMOCHEMISTRY AND THERMODYNAMIC PROPERTIES OF SUBSTANCES[1]

By MARTIN A. PAUL[2]

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Research on thermochemistry and the thermodynamic properties of substances continues to attract the interest of a large number of investigators. Space limitations preclude more than brief notice of many relevant publications, which are summarized in Table I. This table lists various substances investigated and indicates, by means of a code, the properties determined. Thermodynamic properties of solutions are covered by other chapters of this volume, as are cryogenic properties, irreversible thermodynamics, ion exchange and adsorption. The following remarks concern work whose significance is not adequately conveyed through the table.

APPARATUS AND TECHNIQUES

A book published by Calvet & Prat (35) summarizes their original researches on precision microcalorimetry. Using heat compensation methods based on Peltier electric cooling and Joule electric heating, they have successfully measured heats at power levels as low as 0.2 microwatt. A point of major interest is the measurement of kinetic as well as total reaction heats, and the authors have applied their techniques with particular effect to biological systems.

Michels *et al.* (191) have redetermined the triple points of carbon dioxide and argon by platinum resistance thermometry and find them reproducible within 0.001°C.; they propose that these be adopted as auxiliary fixed points for defining the International Temperature Scale. A practical temperature scale for the range 4–300°K., based on a gold-cobalt vs. copper thermocouple, has been described by Fuschillo (90). A redetermination of the specific heat and entropy of saturated helium between 1.8 and 5.0°K. by Hill & Lounasmaa (122) provides data useful for correcting the helium vapor-pressure thermometer. At the other extreme, a new book edited by Campbell (36) contains a wealth of information on high temperature techniques.

Several precision calorimeters have been designed to serve special purposes. A gold calorimeter used to measure the heat capacity of aqueous CsI solutions within 0.03 per cent precision at 25°C. is reported to have a temperature sensitivity of 0.00005° with low heat loss [Kapustinskii, Lipilina & Samoĭlov (142)]. An adiabatic copper-block calorimeter designed by Olette (214) uses transistors to follow the block temperature with a sensitivity of 0.0003°; it is intended for heat capacity measurements on solids and liquids

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[1] The survey of literature pertaining to this review was concluded December, 1957.

[2] John Simon Guggenheim Memorial Fellow, 1957, on leave at the University of California, Los Angeles, California.

TABLE I

THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES

SUBSTANCE	PROPERTY	TEMPERATURE RANGE, °K.	REFERENCE
Inorganic:			
X(g), 54 elements	f*	0–8000	(152)
O$_3$(l)	a	77–174	(25)
O$_3$(g)	f	100–1500	(2)
D$_2$(c)	e	0.3–13	(96)
H$_2$O(l)	a	293–1273	(293, 294)
H$_2$O(in N$_2$O$_5$)	h	273	(172)
He(l)	a, e	1.2–5.0	(122, 145)
A(g)	a	133–297	(132)
F(g)	f	298–5000	(227)
F$_2$(g)	f, m	298–5000	(227, 231)
HF (l,g)	a, c, d, e	303–573	(87)
HF(g), DF(g)	f	298–5000	(227)
Cl$_2$(aq)	p(H$_2$O)	298	(312)
HCl(HCOOH, etc.)	t	298	(196, 272)
HClO$_4$(aq)	h	298	(22)
ClO$_3$F(l)	a, c, d	153–363	(135)
ClO$_3$F(g)	j, l	298	(63, 207)
Br$_3^-$ (aq. CH$_3$COOH)	p	275–298	(203)
BrF$_3$(g)	l, p, s	329–380	(258)
I$^-$(aq), I$_2$(c)	t	298	(234)
S^{34}O$_2$(g)	p(H$_2$S^{32}O$_4$)	478–678	(71)
H$_2$SO$_4$(in HNO$_3$)	h	273	(172)
H$_2$Se(g), HDSe(g), D$_2$Se(g)	f	100–1000	(3)
H$_2$Te(g)	f	100–400	(3)
Po(c,α), Po(c,β)	a, b	179–327	(31, 97)
N$_2$(g)	m	0	(280)
NO$_2$(g)	f	100–1500	(2)
N$_2$O$_5$(g)	k, l	298	(230)
NH$_3$(g)	n	0	(295)
HNO$_2$(g)	f	100–1000	(2)
NH$_4$NO$_3$(c)	b	433–443	(143)
NO$_2$Cl(g)	f	100–1000	(91)
NH$_2$OH·HCl(c)	h, k, p	288–313	(194, 195)
NH$_4$F(c)	e, g	6–309	(14)
H$_3$PO$_4$(c,l)	b, e, o	10–300	(74)
2H$_3$PO$_4$·H$_2$O(c,l)	b, e, o	10–300	(74)
PCl$_5$(g)	f	298–1500	(305)
SbF$_5$(l)	a, c	263–343	(124)
Bi(c)	c	497–532	(205)
Bi$_2$(g)	m	0	(26)
C(graphite)	c	2400	(278)

* See Code to Properties at the end of table.

SUBSTANCE	PROPERTY	TEMPERATURE RANGE, °K.	REFERENCE
$C_2(g)$	m	0, 2400	(70)
$CO(g)$	m	0	(280)
$CO^+(g)$	m, n	0	(188)
$CO_2(l)$	a	292	(233)
$CO_2(g)$	a	213–303	(51)
$COCl_2(g)$	f	298–4000	(98)
$Si(c,l)$	b, e	1473–1823	(215)
$Si_2(g)$	m	0, 1660	(70)
$SiO_2(\alpha\text{-quartz})$	e	10–700	(174)
$SiO_2(\text{vitreous})$	e	10–900	(174)
$SiO_2(\alpha\text{-quartz})$, $SiO_2(\text{amorphous silica})$	h, $r(H_2O)$	298–450	(100)
$SiO_2 \cdot nH_2O(\text{silica gel})$	$k[Ca(OH)_2]$	298	(210)
$SiH_4(g)$	k, l	298, 953	(29)
$SiCl_4(g)$	$p(H_2)$	1173–1573	(187)
$Ge_2(g)$	m	0, 1370	(70)
$GeO_2(c)$	l, $p(H_2)$, s	773–923	(310)
$Sn_2(g)$	m	0, 1200	(70)
$Pb_2(g)$	m	0, 800	(70)
$PbCl_2(l)$	c	950–1180	(13)
$PbS(c)$	s	523–700	(151)
$PbSb_2S_4(c)$, $Pb_3Sb_2S_6(c)$	r	673	(290)
$GaCl_3 \cdot PCl_3(\text{2-phase})$	l	298	(102)
$GaCl_3 \cdot POCl(c)$	l	298	(101)
$InP(c)$	q	973–1318	(297)
$ZnS(c)$	b	2103	(1)
$Zn(NH_3)_2Cl_2(c,aq)$	k, p	298	(271)
$Zn_3As_2(c)$	k, l	298	(7)
$Cd(c)$	e	293–543	(240)
$CdCl_2(l)$	c	940–1190	(13)
$Cu(c,l)$	b	1353–1443	(95)
$Cu(l)$	c	1575–1730	(242)
$Cu_2(g)$	l, m	0, 1530	(70, 242)
$Cu_2O(c)$	s	1073–1323	(151)
$CuH(g)$	m, p	1800–2400	(33)
$CuOH(g)$	m, p	1800–2400	(34)
$CuBr_2(c)$	q, r	424–523	(12)
$Cu_2S(c)$	s	523–623	(292)
$Cu(NH_3)_n^{++}(aq)$, n = 1–5	k	300	(309)
$Cu(NH_3)_4SO_4 \cdot H_2O(c)$	e	0.3–24	(89)
$CuSbS_2(c)$, $Cu_3SbS_3(c)$	r	673	(290)
$Ag(c)$	e	2.0–4.2	(123)
$Ag(l)$	c	1275–1485	(242)
$Ag_2(g)$	l, m	0, 1285	(70, 242)
$Ag_2O(c)$	o, s, t	273–320	(111)
$AgCl(\text{in } KCl\text{—}NaCl)$	t	925–1119	(81, 82)
$AgI(c,\alpha)$, $AgI(c,\beta)$	a, b, e	285–740	(125)

SUBSTANCE	PROPERTY	TEMPERATURE RANGE, °K.	REFERENCE
$Ag_2S(c)$	s	423–698	(151)
$Ag(S_2O_3)_2{}^{3-}(aq)$	l, p, s	298–343	(38, 39)
$Ag_2Se(c)$	s	433–643	(151)
$Ag_2Te(c)$	s	523–573	(151)
$AgSbS_2(c)$, $Ag_3SbS_3(c)$	r	548–673	(290)
$Au(l)$	c	1607–1764	(242)
$Au_2(g)$	l, m	0–1550	(70, 242)
$Pt(c)$	e, o	10–273	(47)
$IrCl_6{}^-(aq)$, $IrCl_6{}^{3-}(aq)$	r, t	288–312	(92)
$OsO_2(c)$, $OsO_4(aq)$	t	298	(37)
$ReO_3(c)$	l, o, s, t	298–308	(149)
$Pd(c)$	e	2.0–4.2	(123)
$RuO_4(aq)$, $RuO_4{}^-(aq)$	p	298	(50)
$NiO(c)$	e, o	51–298	(147)
$NiO(c)$	s	1023–1413	(151)
$Ni(NH_3)_n{}^{++}(aq)$, $n=1$–6	k	300	(309)
$Ni(CO)_4(l,g)$	i, l, s	298	(80)
$CoO(c)$	e, o	51–298	(147)
$CoO(c)$	s	1173–1373	(151)
Co_3O_4(cobalt spinel)	e, o	51–298	(147)
$CoTe_x(c)$, $x=1.0$–2.0	k, l	298	(6)
$Co(CO)_3NO(l)$	c	278–338	(192)
$Fe_3O_4(c)$	p, q, $r(O_2)$	1354–1731	(84, 253)
$FeBr_2 \cdot nH_2O(c)$, $n=1,2,4$	q, r	293–433	(103)
$ZnFe_2O_4(c)$	e, u	5–300	(302)
$Ni_{1-x}Zn_xFe_2O_4(c)$, $x=0.6$–0.9	e, u	5–300	(301)
$MnCl_2 \cdot nCH_3OH(c)$, etc.	k, q	323	(41)
$CrO_3(c)$	h, k	298	(197)
$CrO_4{}^-(aq)$, $Cr_2O_7{}^-(aq)$, $HCrO_4{}^-(aq)$	k, l, o, s	298	(197)
$(NH_4)_2Cr_2O_7(c)$	k, l	298	(208)
$MoO_2(c)$	i, l	298	(175)
$MoO_3(c)$	c, l	298, 1123–1248	(20, 175)
$WO_2(c)$	c	1340–1460	(18)
$WO_3(c, II)$	l, o, p, s	298, 873–1273	(288)
$CuWO_4(c)$	$p(H_2)$	578–1023	(289)
$Fe_xMn_{1-x}WO_4(c)$	$p(H_2)$	1240–1323	(156)
$VO(c,g)$	c, r	1680–1950	(19)
$VF_5(c,l)$	b, c	252–359	(45, 281)
$TaO(g)$, $TaO_2(g)$	p, r	2000–2300	(130)
$TaSi_x(c)$, $x=0.2$–2.0	l, q	1900–2500	(199)
$Ti(c)$	e	1.2–20	(307)
$TiO(c)$, $TiO_2(c)$	c	1700–2100	(21)
$TiO_x(c)$, $x=0.25$–2.0	l	293	(8)
$TiO_2(c)$	p(C, CO)	1880–2600	(157)
$TiCl_2(c)$, $TiCl_3(c)$	l, o, p	298, 813–973	(117)
$TiCl_3$(in NaCl-KCl)	p(Ti)	973–1073	(154)
$TiBr_4(c)$	l	298	(243)

SUBSTANCE	PROPERTY	TEMPERATURE RANGE, °K.	REFERENCE
$Zr(c)$	e	1.2–20	(307)
$Zr(c)$, $ZrO_2(c)$	c	2300–2500	(42)
$ZrF_4(c)$	c	889–1154	(246)
$ZrCl_4(c)$	l	298	(105)
$Hf(c)$	e	1.2–20	(307)
B(amorphous)	c	2115–2413	(245)
$B_2O_2(g)$	l, p	298, 1337–1375	(245)
$B_2O_3(c)$	c	1501–1566	(245)
$B_5H_9(l)$, $B_5D_9(l)$	c	225–330	(249)
$H_3BO_3(aq)$	h	298	(165)
$BF_3(g)$, $BF_3{}^+(g)$, $BF_2{}^+(g)$	n	0	(153)
$NH_4B(C_6H_5)_4(c)$	e, o	20–298	(58)
$Al(c,l)$	b	933–1053	(95)
Al_2O_3(corundum)	l, e	298–700	(175, 299)
$Al_2O_3 \cdot H_2O$(boehmite)	k($-H_2O$)	773	(190)
$Al_2O_3 \cdot 3H_2O$(hydrargillite)	k($-3H_2O$)	503	(189)
$Al_2O_3 \cdot 3H_2O$(bayerite)	k($-3H_2O$)	483	(189)
$AlF_3(c)$	e, o	51–298	(146)
$AlCl_3(aq)$	h	298	(166)
$AlN(c)$	l	298	(209)
$Y_2O_3(c)$	l	298	(127)
$Tm(c)$	c	809–1219	(257)
$Ho(c)$	e, g	15–300	(93)
$Ho_2O_3(c)$	l	298	(128)
$Tb(c)$	e, o	15–350	(136)
$Ce(c)$	b	286–291	(94)
$Ce(c)$, $La(c)$	e	1.5–20	(220, 237)
$AmO_2{}^+(aq)$, $AmO_2{}^{++}(aq)$	k, l	298	(107)
$UO_2{}^{++}(aq)$	p(H_2O)	298–313	(119)
$U_4O_9(c)$	e, g	5–310	(216)
$UH_3(c)$	l, q	723–923	(170)
$UF_4(c)$, $UF_6(c)$	k(H_2O)	305	(226)
$UF_4 \cdot 2.5H_2O(c)$	k, q	293–318	(225)
$UO_2F_2(c)$	k, l	305	(226)
$UO_2(NO_3)_2(aq)$	h	298	(166)
$UCl_4(c)$	h	298	(119)
$UO_2(C_2H_3O_2)_2(aq)$	h	298	(241)
$ThO_2(c)$	r	928–1233	(254)
$ThCl_4(l)$	l, s	298, 928–1233	(254)
$Th(NO_3)_4(aq)$	h	298	(166)
$BeO(c)$, $BeCl_2(l)$	t	973–1173	(255)
$Mg(c)$	e	293–543	(240)
$MgP_2O_7{}^-(aq)$	k, p, r	298	(163, 287)
$Mg_3As_2(c)$	k, l	298	(7)
$Mg_3Cd(c)$	e	4–15	(17)
$Mg_3Cd(c)$, $MgCd_3(c)$	e, l, o, s, v	293–563	(137)
$MgB_2(c)$, $MgB_4(c)$	e, o	18–305	(270)

Substance	Property	Temperature Range, °K.	Reference
$Ca(c)$, $Sr(c)$, $Ba(c)$	e, g	1.5–20	(235)
$Ca(OH)_2(c)$	q	635–777	(110)
$Ca_2P_2O_7(c,l)$	b, e, o, u	10–1700	(73)
$Ca(H_2PO_4)_2 \cdot H_2O(c)$	h	298	(72)
$CaCO_3(c)$	q	722–1177	(120)
$Ca_2SiO_4(\alpha,\alpha',\beta,\gamma)$	b, e, o, u	51–1800	(54, 148)
$Ca_2Si_2O_7(c)$	e, o	51–298	(148)
$CaAl_2Si_2O_8$(anorthite)	e, o	51–298	(148)
$CaMgSi_2O_6$(diopside)	e, o	51–298	(148)
$Ca_3[Fe(CN)_6]_2(aq)$	h	298	(167)
$Ca_2Fe(CN)_6(aq)$	h	298	(167)
$Sr_3P_2(c)$	k, l	298	(250)
$Sr_3As_2(c)$	l	298	(5)
$SrSb(c)$, $Sr_3Sb_2(c)$, $Sr_3Sb(c)$	l	298	(251)
$SrSiO_3(c)$, $Sr_2SiO_4(c)$	k, l	298	(11)
$Sr_3[Fe(CN)_6]_2(aq)$	h	298	(167)
$Sr_2Fe(CN)_6(aq)$	h	298	(167)
$Ba_3Bi_2(c)$	k, l	298	(252)
$BaSi_2O_5(c)$, $Ba_2Si_3O_8(c)$, $BaSiO_3(c)$, $Ba_2SiO_4(c)$	k, l	298	(11)
$Li(c)$, $Na(c)$, $K(c)$	e, g	1.5–20	(236)
$Li_3As(c)$, $Li_3Bi(c)$	k, l	298	(7, 252)
$LiBO_2(c,l)$	b	1109	(222)
$LiAlO_2(c)$	l	298	(53)
$NaF(c)$	e, o	51–298	(146)
$NaF(c,l)$	b, c, e, g	298–1746	(164, 213, 247)
$NaCl(c)$	c	743–948	(206)
$NaCl(l)$	c	1330–1540	(13)
$Na_3Fe(CN)_6(aq)$	h	298	(168)
$NaBO_2(c,l)$	b	1239	(222)
$Na_2B_4O_7(c)$	e, g, o, s	6–350	(300)
$Na_2B_4O_7$(vitreous)	e, u	6–350	(300)
$NaAlO_2(c)$	l	298	(53)
$Na_3AlF_6(c,l)$	b, e, o, u	51–1370	(146, 164, 213)
$K(c)$	e, o	12–320	(155)
$KCl(l)$	c	1280–1540	(13)
$KNO_3(c)$	b	607	(68)
KNO_3(in HNO_3)	h	273	(172)
$K_3Sb(c)$, $K_3Bi(c)$	l	298	(193)
$K_2MnO_4(aq)$	k, l	273	(121)
$K_2CrO_4(c)$, $K_2Cr_2O_7(c)$	h, k, l	298	(197)
$KB(C_6H_5)_4(c)$	e, o	20–298	(58)
$Na_2K(c)$	e, o	12–320	(155)
$RbCl(c)$	c	678–868	(206)
$RbB(C_6H_5)_4(c)$	e, o	20–298	(58)
$CsI(aq)$	e	298	(142)
$MX(g)$, alkali halides	f	298–2000	(232)

Substance	Property	Temperature Range, °K.	Reference
MX(l), alkali halides	a	873–1273	(23)
MNO$_3$(l), alkali nitrates	a	573–773	(23)
M$_2$MoO$_4$(c,l) alkali molybdates	b	Varied	(223)
Organic:			
CCl$_4$(l), CHCl$_3$(l), CH$_2$Br$_2$(l), CH$_3$I(l)	a, e	243–303	(115, 233)
CHClF$_2$(c,l)	b, c, e, g	16–233	(204)
CH$_3$(g), CD$_3$(g), CD$_4$(g), C^{14}H$_4$(g)	p	300–600	(56)
CH$_3$ONa(c)	e, g	5–345	(104)
trans-CClF=CClF(g)	f	200–1500	(176)
CF$_2$=CBr$_2$(g)	f	350–600	(275)
CF$_3$CN(g), CClF$_2$CN(g), CCl$_2$FCN(g), CCl$_3$CN(g)	f	298–1500	(134)
CF$_2$=CHBr(g)	f	298–800	(276)
CF$_3$—CHBrCl(g)	f	330–1000	(277)
CClF$_2$—CH$_2$Cl(l)	a, c	355–498	(61)
CF$_3$—CH$_2$Br(g)	f	310–1000	(212)
cis- and *trans*-CHBr=CHBr(g)	f	100–1000	(69)
cis- and *trans*-CDBr=CDBr(g)	f	100–1000	(69)
CHCl$_2$—CH$_2$Cl(l,g)	c, e	330–474	(304)
CHCl$_2$—CH$_2$Cl(g)	f	273–1500	(116)
CHBr=CH$_2$(g)	j, l	298, 401	(158)
CH$_3$—COF(l)	c	90–221	(269)
CH$_3$—COF·BF$_3$(c)	q, r	195–273	(269)
CH$_3$—COSH(l)	k, l	298	(268)
C$_2$H$_5$ONO$_2$(l)	i, l	298	(79)
C$_2$H$_5$SH(l,g)	c, f, i, l	298–1000	(184)
CH$_3$—S—CH$_3$(l,g)	c, e, f, i, l	298–1000	(184)
(CNCl)$_3$(c)	k, l	353	(129)
C$_3$H$_3$$^+$($g$)	l, n	298	(49)
CH$_2$=C=CH$_2$(g)	m, n	298	(49)
C$_3$H$_6$, propylene (g)	k(HBr)	401	(162)
C$_3$H$_6$, propylene (in butadiene)	k(SO$_2$)	300	(55)
C$_3$H$_6$, cyclopropane (g)	k(HBr)	401	(162)
(CH$_2$)$_3$O, trimethylene oxide (g)	f	298–1000	(313)
CH$_3$—CO—CH$_3$(l,g)	c, e, g, o	298–1500	(221)
n- and *iso*-C$_3$H$_7$F(g)	j	521	(160)
n- and *iso*-C$_3$H$_7$ONO$_2$(l)	c, i, l	273–343	(79, 99)
n- and *iso*-C$_3$H$_7$OH(l)	c	323–353	(304)
C$_3$H$_5$(OH)$_2$OPO$_3$Na$_2$, disodium glycerol 1- and 2-phosphates (c)	i, l	298	(46)
(CH$_3$)$_3$As(l)	i, l	298	(173)
C$_4$F$_8$, *n*- and *iso*-perfluorobutene-1	k(Cl$_2$)	401	(161)
(CF$_3$—COOH)$_2$(g)	m	298–373	(141)
C$_4$H$_4$O$_4$, fumaric and maleic acids (in CH$_3$COOH)	h, j	298	(83)
C$_4$H$_6$, cyclobutene (g)	f	276–1500	(57)

Substance	Property	Temperature Range, °K.	Reference
(CH$_3$)$_2$SI$_2$(in CCl$_4$), (CH$_3$)$_2$SeI$_2$(in CCl$_4$)	p	298	(279)
(CH$_3$CO)$_2$O$_2$(l)	i, l	298	(133)
t-C$_4$H$_9$Br(g)	e, l, o, p	298–700	(126)
n- and iso-C$_4$H$_9$ONO$_2$(l)	c	273–343	(99)
C$_4$H$_{10}$S, 1-butanethiol and 2-thiapentane (c,l,g)	b, c, e, f, g, i, l	12–1000	(244)
C$_5$F$_{10}$, perfluoropentene-1 (g)	k(Cl$_2$)	401	(161)
C$_5$H$_5$N, pyridine (c,l,g)	b, c, e, f, g, l, s	10–1500	(169, 181)
C$_5$H$_5$N, pyridine (g)	k, p, r(H$_2$)	413–533	(108)
C$_5$H$_8$O$_2$, acetylacetone (l)	i	298	(211)
C$_6$F$_{12}$, perfluorocyclohexane (l)	c	293–393	(238)
C$_6$H$_{10}$O$_2$, ethyl methacrylate (g)	k, p	375–411	(52)
(CH$_3$—CH$_2$—CO)$_2$O$_2$ (l)	i, l	298	(133)
C$_6$H$_{11}$ON, ϵ-caprolactam (aq)	p(H$_2$O)	473–573	(186)
C$_6$H$_{11}$O$_9$PO$_4$K$_2$, dipotassium glucose 1-phosphate (c)	i, l	298	(46)
C$_6$H$_{12}$, hexene-1 (in CH$_3$COOH)	h, j	298	(83)
Seven 1-olefins, C$_6$H$_{12}$–C$_{16}$H$_{32}$(g)	b, e, o	10–360	(182)
(SCH$_2$—CHNH$_2$—COOH)$_2$, cystine (aq)	p	310	(77)
(C$_2$H$_5$O)$_3$P(l)	k(S)	298	(40)
Six fluorocarbons, C$_7$F$_{14}$(l), etc.	e	298–383	(308)
o-C$_6$H$_4$(OH)COOH, salicylic acid (aq)	k, p, r	297–328	(10)
C$_7$H$_6$O, tropone (in CH$_3$COOH)	j	298	(283)
C$_6$H$_5$—CH$_2$Br(g)	l, p(HBr)	423	(15)
C$_8$H$_{10}$, 1,7-octadiyne (in CH$_3$COOH)	h, j	298	(83)
C$_8$H$_{10}$, dimethylfulvene (l)	i	298	(59)
Eight methyl-substituted benzenes, C$_8$H$_{10}$–C$_{12}$H$_{18}$(g)	f, l, o, s	298–1000	(118)
Sixteen cyclic and bicyclic hydrocarbons (bicyclo[2,2,2]octadiene, azulene, cyclodecene, etc.)	j	298	(282, 283, 284)
(n-C$_2$H$_7$CO)$_2$O$_2$(l)	i, l	298	(133)
C$_8$H$_{23}$N$_5$, tetraethylenepentamine(aq)	k	298	(138, 139)
C$_9$H$_6$O$_2$, coumarin(aq)	p(H$_2$O)	298	(179)
C$_9$H$_{12}$, 1,2,4-trimethylbenzene(c,l,g)	b, e, o	15–300	(229)
(n-C$_3$H$_7$)$_3$P(l)	k(S)	298	(40)
C$_{10}$H$_8$, naphthalene (c) and five substituted derivatives	b, e, g	12–370	(183)
C$_{10}$H$_{17}$O$_6$SN$_3$, glutathione (aq)	p	310	(77)
C$_{11}$H$_{23}$COOH, lauric acid (c)	c	293–313	(171)
C$_{12}$H$_{18}$, 3,9- and 5,7-dodecadiyne (in CH$_3$COOH)	h, j	298	(83)
(n-C$_4$H$_9$)$_3$P(l)	k(S)	298	(40)
C$_{14}$H$_{12}$O$_3$, $trans$-stilbene ozonide (c)	i	298	(30)
C$_{13}$H$_{14}$, diphenylfulvene(c)	i	298	(59)
ATP, adenosine triphosphoric acid (aq)	p, r(H$_2$O)	298	(291)

SUBSTANCE	PROPERTY	TEMPERATURE RANGE, °K.	REFERENCE
Six steroid olefins (cholest-1-ene, etc.)	j	298	(285)
Fifteen amines [$CH_3NH_2(g)$, $(CH_3)_2NH$ (g), $C_6H_5NH_2(g)$, etc.]	n	0	(295)
Twenty-six derivatives of urea, diphenylamine	i, l	293	(273)
Nitroglycerol and eight related di- and trinitroxy compounds	c	293–313	(144)
Thirteen explosive nitro compounds, nitrates, nitramines	i, l	291	(185)
Thirty-eight triazoles, tetrazoles and related compounds	i, l	298	(303)
Fourteen cyclic hydrocarbons and heterocyclic nitrogen compounds	d	—	(4)
Twenty esters of phosphoric and phosphonic acids	c	Varied	(67)
Twenty-four hemiacetals	e, k	298	(9)
Seven odoriferous compounds (benzyl alcohol, eugenol, etc.)	c	283–343	(248)
Cellobiose, cellotriose	h	298	(274)
Coal tars, pitches and coal tar distillates	e	293–483	(27, 28)

CODE TO PROPERTIES IN TABLE I

a. Density, compressibility, equation-of-state data.
b. Cryoscopic or other phase-transition data.
c. Vapor pressure, heat of vaporization or sublimation.
d. Critical state data.
e. Heat capacity.
f. Thermodynamic functions, ideal gas state [usually C_P^0, $(H^0 - H_0^0)/T$, $-(F^0 - H_0^0)/T$, S^0].
g. Thermodynamic functions, liquid, or solid state [usually C_P^0 or C_P^{std}, $(H^0 - H_0^0)/T$ or $(H^{std} - H_0^0)/T$, etc.].
h. Heat of solution or dilution.
i. Heat of combusiton.
j. Heat of hydrogenation.
k. Heat of a reaction.
l. Standard enthalpy of formation (usually at 298°K.).
m. Dissociation energy or enthalpy.
n. Ionization potential or appearance potentials for ions.
o. Standard entropy, S^0, or entropy increment, $S^0 - S_0^0$ (usually at 298°K.).
p. Equilibrium data for a reaction.
q. Dissociation pressure.
r. Standard free energy of a reaction.
s. Standard free energy of formation.
t. Standard cell or electrode potential for a reaction.
u. Enthalpy and entropy increments
v. Order-disorder transition data.

up to 1600°C. and data are reported for crystalline and liquid silicon (215). Egupov (76) describes a precision calorimeter of small volume and low energy input, without stirring, for measuring heat capacities of liquid solutions close to their critical solution temperatures. An all-glass precision calorimeter containing an inert atmosphere has been designed by Greenwood & Perkins (101) to measure reaction heats for such hygroscopic and corrosive substances as POCl (l) and GaCl$_3$(c).

Lacher *et al.* (159) have described an isothermal gas-flow calorimeter with which they have studied the heats of catalytic hydrogenation and chlorination reactions of organic compounds. The reaction vessel containing palladium-on-carbon catalyst is immersed in a volatile liquid cooled at a known rate by evaporation into an inert gas. The flow of the inert gas is regulated until the cooling rate just compensates for the rate of heat evolution from the reaction vessel.

Enthalpy titrations are reported by Jordan & Ben-Yair (140). The reactants are combined in a Dewar flask and the temperature is followed with change in the molal proportion. Since $\Delta H = \Delta F + T \Delta S$, the magnitude of the observed effect depends on an entropy change as well as the free-energy change followed in ordinary potentiometric titrations. One of the systems investigated is Zn^{++} vs. tartrate in aqueous solution, breaks occurring at both 1:1 and 1:2 molal proportion of zinc to tartrate.

State Data

State and thermodynamic data for selected gases have been compiled in a new series of publications edited by Din (65, 66). An equation of state for gases based on series expansions in terms of orthogonal polynomials is described by Pings & Sage (224); the coefficients are said to be easily evaluated from the experimental data with the aid of a digital computer and the method is illustrated in detail for propane.

Several investigations have been reported on compressibilities determined from ultrasonic sound velocity measurements. Bockris & Richards (23) have studied alkali halide and nitrate salts at elevated temperatures while Owen & Simons (218) have determined partial molal compressibilities for some dilute aqueous salt solutions at 25°C. Richardson & Tait (233) have studied a number of organic liquids at static pressures up to 700 atm. Working with somewhat more vigorous shock waves generated by high explosives, Walsh & Rice (293) have measured the compressibilities of a variety of liquids including water. They have tabulated the thermodynamic properties of liquid water up to 3150°C. and 450 kilobars (294) and give an equation of state applicable over the range, 20 to 1000°C. and 25 to 250 kilobars.

A series of phase studies at low temperatures and high pressures (to 10,000 atm.) is reported by Stevenson (259, 260, 261). Substances investigated include crystalline O_2, CO, CO_2, CS_2, COS, CH_4, and H_2S; a new crystalline phase of methane has been found at liquid-helium temperatures and

pressures exceeding 2000 atm. (260). Gonikberg, Shakhovskoi & Butuzov (95) have followed the melting points of aluminum and copper to a pressure of 18,000 atm., observing that the change with pressure is practically linear for both metals.

The theory of thermal transformations in solids has been reviewed by Ubbelohde (286), who notes that when one solid is generated within a matrix of another, the concept of independent phases needs reconsideration. In particular, the state of each phase may depend on variables ordinarily neglected, such as strain energy, and this may modify the form of the phase rule as applied to such systems.

Empirical density-pressure-temperature relationships for liquid hydrocarbons are described by Francis (85), who has also given a correlation of critical temperatures for pure hydrocarbons with their normal boiling points (86). Maxwell & Bonnell (180) offer a linear method of correlating the vapor pressures of pure liquid hydrocarbons and their mixtures while Othmer *et al.* (217) give correlation constants for a large number of organic compounds in the semiempirical linear equation relating log p to its value for a reference substance at the same temperature.

Devyatykh (62) has calculated isotope effects for D^2, C^{13} and O^{18} on the triple-point vapor pressures of methane and water; the results are in general, though not exact, agreement with the observed effects.

A study of the freezing points of liquids (benzene, dioxane, etc.) on porous solids shows that they may be lowered by as much as 50°, to an extent depending on pore dimensions [Puri, Singh & Myer (228)]. The observed effects are consistent with the Kelvin equation relating vapor pressure to surface curvature on the supposition that the vapor pressure of the liquid is lowered but not that of the solid.

Heat Capacities

Heavy irradiation of graphite in a nuclear reactor for several years results in a low temperature heat capacity appreciably larger than that of normal graphite [De Sorbo & Tyler (60)]; the effect is attributable to interplanar atoms or clusters giving rise to vibrational modes of low frequencies. A calculation of the heat capacity for α-quartz from its vibrational spectrum has given results between 10 and 700°K. in excellent agreement with experiment [Lord & Morrow (174)]; fair agreement was obtained also for vitreous silica on the basis of an estimated distribution of low frequencies. The heat capacities of the ammonium, potassium, and rubidium salts of tetraphenyl boron were measured between 20 and 298°K. by Davies & Staveley (58) in an attempt to establish the existence of free rotation of the ammonium ion in the relatively open lattice afforded by the large anion. While the values for the ammonium salt were somewhat larger than for the rubidium salt, the difference was entirely within a range attributable to torsional oscillations without free rotation.

Nace & Aston (200, 201, 202) have measured the heat capacity of palla-

dium "hydride" between 16 and 340°K. and also the equilibrium hydrogen pressure from 273 to 345°K. They compute a residual entropy for $Pd_2H(c)$ at 0°K., of 0.59 e.u. mole^{-1}, and conclude from the indicated lack of complete order that the "hydride" is not a true compound. From the shape of the heat capacity curve they infer that hydrogen is nevertheless covalently bound at low temperatures.

Halford & Miller (109) have used a thermal conductivity method to determine C_V^0 for gaseous methane, ethane, methanol, and ethanol; the measurements were at 279°K. and pressures of the order 10^{-3} mm.Hg.

The difference between C_P and C_P^0 with changing pressure for different gases can be represented with reasonable precision as a universal function of reduced temperature and reduced pressure; empirical graphs for the purpose have been prepared by Weiss & Joffe (298). A rule analogous to Dühring's vapor-pressure rule has been applied to other thermodynamic functions such as C_P^0 and $(H^0 - H_0^0)/T$ by Erdös & Černy̆ (78); they note that if T' and T'' denote temperatures at which two different substances, more or less similar in structure, attain the same value for the given thermodynamic property, then with change in the value of the property the corresponding changes in T' and T'' are approximately linearly related to each other. Empirical formulas and tables for the heat capacities of solid n-paraffins between 12 and 300°K. have been compiled by Maslov (177).

Thermochemical and Related Data

Two groups of investigators have recently undertaken calorimetric measurements on catalytic hydrogenation reactions in liquid solutions. Flitcroft, Skinner & Whiting (83) have studied fumaric and maleic acids and also several diacetylenes, using ethanol and acetic acid as solvents and PtO_2 as catalyst at 25°C.; they also determined heats of solution so that corrections could be made to standard states for the pure compounds. Turner *et al.* (282 to 285), using acetic acid as solvent, have studied a large variety of cyclic and bicyclic nonbenzenoid hydrocarbons, including several steroid olefins. They have used the results to calculate resonance energies for various ring configurations.

Papee, Canady & Laidler (219) report a redetermination of the heats of neutralization of sulfuric and hydrochloric acids by sodium hydroxide; corrected to infinite dilution at 25°C., the results are respectively 13.48 and 13.52 kcal. per mole of H_2O produced.

Lange and his co-workers (165 to 168) have obtained precise heats of dilution for a number of salts and other compounds in aqueous solutions and from some of the anomalies observed have drawn inferences concerning the chemical states. For example, $Na_3Fe(CN)_6$ is in excellent agreement with the Debye-Hückel theory for a strong 3:1 electrolyte but $Ca_3[Fe(CN)_6]_2$ and $Sr_3[Fe(CN)_6]_2$ show marked deviations from the theory. It is inferred that significant concentrations of intermediate ions such as $CaFe(CN)_6^-$ are present. On similar evidence, Salman & White (241) find that it is impossible

to regard uranyl acetate as a simple strong electrolyte in dilute aqueous solutions.

Among less common methods of measuring reaction energies, reflected shock wave studies have been used to determine dissociation energies for $N_2(g)$ and $CO(g)$ at temperatures up to 10,000°K. [Toennies & Greene (280)]. A study of the temperature dependence of the OH stretching bands in the infrared absorption spectrum of gaseous trifluoroacetic acid has given the enthalpy of dissociation for dimer to monomer [Kagarise (141)]. Hargreaves (112, 113, 114) has analyzed the effect of temperature on optical rotatory dispersion to calculate the enthalpies of transition between optical isomers; those of 1,2-diphenylethanol for example.

Bulewicz & Sugden (33, 34, 267) have undertaken photometric studies of chemical equilibria produced in flames. By varying the flame temperature, the corresponding reaction enthalpies may be determined and they have thus measured the dissociation enthalpies of $CuH(g)$ and $CuOH(g)$. Broida & Shuler (32) have found that the relative intensities of lines in the electronic spectrum of iron serve as a satisfactory flame temperature indicator over regions where thermal equilibrium exists; iron is conveniently fed into the flame in the form of ferrocene.

Continuing a study of high temperature flames, Stokes & Grosse (262) note that a flame of composition $2HCN:O_2:F_2$, based on materials all now commercially available, yields a maximum temperature at 1 atm. of about 4000°K. This almost equals the theoretical maximum for the $H_2:F_2$ flame, though it is well below the value of 4856°K. calculated for the $(CN)_2:O_2$ flame. A theoretical value of 5208° K. at 1 atm. is obtained for the $3(CN)_2:2O_3$ flame [Streng & Grosse (265)].

Borchardt (24) has criticized the dynamic gas method of differential thermal analysis as applied by Stone (263, 264) to measure the heats of such reactions as the decomposition of magnesite, $MgCO_3$; he notes that the temperature of the sample may depend on kinetic factors and does not necessarily agree with the equilibrium temperature corresponding to the partial gas pressure maintained in the sample holder.

APPLICATIONS OF MASS SPECTROMETRY

A recent development of considerable interest is the application of the mass spectrometer to problems bearing on chemical thermodynamics. Two distinct types of information can be obtained: (a) the mass spectrometer may be used simply to analyze the equilibrium compositions of gases under conditions inaccessible with the same degree of precision by other means; a case in point is the analysis of the vapor phase obtained from refractory solids in Knudsen effusion studies; (b) appearance potentials, determined for various ionic species, can in many instances be directly translated into thermochemical data.

Continuing their program of examining the vapors from refractory solids by a combination of Knudsen and mass spectrometric techniques, Inghram,

Chupka & Berkowitz have recently studied the oxides of tungsten (18), molybdenum (20), and vanadium (19). In each case polymeric species predominated in the vapor phase. For $WO_3(c)$ at 1492°K. the principal species was W_3O_9 with W_4O_{12} and W_5O_{15} also present at lower concentrations. The behavior of $MoO_3(c)$ was similar and in both cases heats of sublimation could be determined for the various species from their partial vapor pressures. For $V_2O_5(c)$ the principal vapor constituents were V_4O_{10}, V_6O_{14} and V_6O_{12} but the composition varied with time. For $VO(c)$ the species V and VO_2 were found as well as VO; these presumably arise through the disproportionation, $2VO(g) = V(g) + VO_2(g)$, whose equilibrium constant (at 1945°K.) could be computed from the data.

These investigators have also observed ZrO as well as Zr and ZrO_2 in the vapor from a mixture of $Zr(c)$ and $ZrO_2(c)$ at temperatures of 2100 to 2300°K. (42), TiO from a mixture of $Ti(c)$ and $TiO_2(c)$ at 1700 to 2100°K. (21), and both TaO and TaO_2 from a mixture of $Ta(c)$ and $Ta_2O_5(c)$ at 2000 to 2300°K. (130). Since tantalum because of its own low volatility is often used as a material for Knudsen cells, these results suggest caution in interpreting the data where oxides are concerned.

The predominance of C_3 in the vapor from graphite previously established from mass spectrometric observations by Chupka & Inghram (43) has been confirmed by Thorn & Winslow (278) from measurements of both the total rate of sublimation from a graphite surface and the effusion rate from an orifice in a graphite cavity. Also the species B_2O_2 detected with the mass spectrometer by Inghram, Porter & Chupka (131) in the vapor from a mixture of boron and boric oxide is reported to be formed by the reaction, $2B(s) + 2MgO(c) = B_2O_2(g) + 2Mg(g)$, when amorphous boron and crystalline magnesium oxide are heated together in a Knudsen cell at 1337 to 1375°K. [Searcy & Myers (245)].

The dissociation energies of diatomic molecules for a number of the metallic elements have been determined by Drowart & Honig (70) from changes in the mass spectrometric ion intensities with temperature. The same quantities may be derived independently from the heats of sublimation at 0°K. of monomer and dimer; these in turn may be calculated from partial vapor pressures observed at a single temperature together with the spectroscopically determined partition functions. Dissociation energies obtained by both methods are compared by these investigators. The partial vapor pressures of monomeric and dimeric molecules in equilibrium with liquid copper, silver, and gold have been determined also by Schissel (242) using Knudsen effusion and analyzing the dimer-monomer abundance ratios with a mass spectrometer.

An application of appearance potentials to a thermochemical problem is found in a study of perchloryl fluoride decomposition [Dibeler, Reese & Mann (63)]. According to the relative abundance measurements, the appearance of Cl^+ ions from this compound follows upon complete disintegration of the molecule into atoms: $ClO_3F(g) = 3O(g) + F(g) + Cl(g)$. Therefore, by sub-

tracting the ionization potential for $Cl(g)$ from the observed appearance potential for $Cl^+(g)$, one obtains directly the energy of the atomization reaction. The result is in good agreement with recent thermochemical data [Neugebauer & Margrave (207)].

Coats & Anderson (48) report a series of electron impact and appearance potential measurements for ions derived from acetylene and various substituted derivatives. From such data they compute, for example, an enthalpy of formation for the free radical $C_2H(g)$. From similar studies with allene and the isomeric butadienes, Collin & Lossing (49) report enthalpies of formation for $C_3H_3(g)$ and $C_3H_3^+(g)$. Friedman, Long & Wolfsberg (88) have undertaken a detailed analysis of relative abundances and appearance potentials for ions derived from the lower alcohols (methanol, ethanol, *n*- and *iso*-propanol). From such studies valuable thermodynamic information can be obtained for transient species postulated as reaction intermediates.

Free Energy and Related Equilibrium Data

Kiukkola & Wagner (150) have surveyed galvanic cells practical for measuring standard free energies of formation of metal halides, oxides, and sulfides at high temperatures. A typical cell with which the free energies of formation for $CoO(c)$, $NiO(c)$, and $Cu_2O(c)$ were determined (151), is the following:

$$Fe(c), FeO(wüstite) | 0.85ZrO_2 - 0.15CaO(c) | Metal(c), Oxide(c).$$
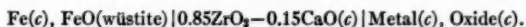
The electrolyte is a solid solution of zirconium and calcium oxides which conducts principally by $O^=$ ion migration through oxygen vacancies. Since the standard free energy of formation for wüstite has been well established as a function of temperature from experimental studies of its reduction equilibrium with $CO(g)$, the only other quantity on which the cell emf. depends is the standard free energy of formation of the other metal oxide. For $Ag_2S(c)$, the cell employed was:

$$Ag(c) | AgI(c) | Ag_2S(c), S(l), C(graphite)$$
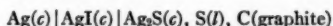
in which the solid silver iodide electrolyte conducts principally through Ag^+ ion migration. The cell reaction is therefore simply the formation of silver sulfide from its elements, $2Ag(c) + S(l) = Ag_2S(c)$. Other types of cells have been devised to measure the free energies of formation of $Cu_2S(c)$ [Wagner & Wagner (292)] and various double sulfides of geochemical interest such as $Ag_3SbS_3(c)$ [Verduch & Wagner (290)].

With high temperature cells of somewhat more conventional design using chloride salts dissolved in 1:1 KCl-NaCl as liquid electrolytes, Flenglas & Ingraham (81, 82) have studied the displacement reactions of zinc, nickel, cobalt, and lead toward silver. Smirnov & Ivanovsky (254) have studied the reduction of $ThO_2(c)$ by carbon and also the free energy of formation of $ThCl_4(l)$ using a high temperature cell with $ThCl_4$ dissolved in eutectic LiCl-KCl as electrolyte.

An unusual type of galvanic cell is described by Russell & Sienko (239) with sodium dissolved in liquid ammonia as the electrolyte. The data lead to the free energy of the reaction, $Na(c) = Na^+(NH_3) + e^-(NH_3)$, that is, to the free energy of formation of $Na^+(NH_3)$ accompanied by electrons instead of anions.

In an analysis of the equilibrium data for $O_2(g)$ over iron oxide spinels, $Fe(II)Fe(III)_2O_4(c)$, Flood & Hill (84) show that if an equilibrium is postulated within the crystal among iron atoms in both states of oxidation, lattice defects and vacancies (since addition of O^- ions upon oxidation creates new cation sites), then an expression for the oxygen pressure can be derived which gives the correct variation with temperature; one does not obtain such an expression from the assumption of independent crystalline phases, $FeO(c)$, $Fe_3O_4(c)$, $Fe_2O_3(c)$. This system has recently been studied experimentally by Smiltens (253).

The reduction of $WO_3(c)$ and several metallic tungstates by $H_2(g)$ has been the subject of a series of equilibrium investigations by Gerasimov *et al.* (156, 288, 289). They find that at temperatures above 873°K., the reduction proceeds through successive stages with compositions $WO_{2.90}$, $WO_{2.72}$ and WO_2 before tungsten itself is reached as the end product.

The solubility products and corresponding standard free energy differences for many metal sulfides and halides have been compiled by Egorov (75) and expressed in terms of empirical formulas over the range 0–100°C. Diebel & Swinehart (64) have tabulated the entropies of ionization for a large number of organic acids in aqueous solutions. They note that -20 e. u. mole^{-1} is the typical order of magnitude, reflecting the orientation of water molecules about the ions, but that values half as large in magnitude are observed in the case of *zwitterions*. The *zwitterion* evidently is itself capable of orienting water molecules to some degree about its charged functional groups; this effect is particularly noticeable when the two groups are sufficiently far apart so that each can behave independently of the other, as in the case of sulfanilic acid ($\Delta S_{298}^0 = -0.37$ e. u. mole^{-1}).

An interesting proposal for presenting free energy and other thermodynamic data in donor acceptor form is advanced by Bent (16). In the case of silver compounds, for example, he would list such silver-ion donors as $AgClO_4(c)$, $AgNO_3(c)$, $AgCl(c)$, $Ag(S_2O_3)_2^{-3}(aq)$, etc., in order of increasing ΔF^0 for the reaction, Ag^+-donor $= Ag^+(aq) + Ag^+$-acceptor, setting up in effect a free energy-level diagram for the reactions of $Ag^+(aq)$. Such species as $ClO_4^-(aq)$, $NO_2^-(aq)$, $Cl^-(aq)$, $S_2O_3^-(aq)$, etc., serve as conjugate acceptors for these reactions. Similar diagrams can be constructed for other reactants and they may be easily modified to take account of concentration changes.

Empirical formulas for the entropies of gaseous and liquid thioalkanes and alkanethiols are given by Maslov (178). A proposed assignment of additive $\log K_f$ and ΔF_f^0 values for organic structural groups is offered by Ciola (44). This would permit the calculation of approximate equilibrium conditions where experimental data are lacking, by taking advantage of the

fact that much of the structure in the reactions of organic molecules persists unchanged; one therefore has only to take differences between log K_f contributions for those structural groups actually affected by the reaction under consideration.

GENERAL

New editions have appeared of several well-known books on thermodynamics [Guggenheim (106), Weber & Meissner (296), Zemansky (311)] while new books on statistical thermodynamics have been published by Münster (198) and by Wilson (306). Thermodynamic data for the first ninety-two elements in their various states of aggregation are compiled in a recent publication by Stull & Sinke (266). The reader's attention is called to the excellent review of thermodynamic data published annually by *Industrial and Engineering Chemistry* [Smith (256)].

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CRYOGENICS[1]

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Following the custom of previous authors of this series we have restricted this review to a few selected topics. In doing so, we have omitted discussion of many important developments in low temperature physics; for example, the crucial experiments at the National Bureau of Standards in which the asymmetry of β decay from polarized Co^{60} nuclei first revealed the breakdown of the concept of parity conservation for weak elementary particle interactions [Wu *et al.* (1)]. Fortunately, many good review articles are available in this expanding field of cryogenics. In particular, we call attention to the *Progress in Low Temperature Physics* volumes edited by Gorter, covering a wide range of topics, and the excellent articles in the *Handbuch der Physik* (2, 2a).

The extent of the interest in cryogenics was underscored in August, 1957, when 440 scientists attended the Fifth International Conference on Low Temperature Physics and Chemistry, at the University of Wisconsin. During the six-day conference, 198 contributed papers and 27 invited papers were presented. The Proceedings, which are being published by the University of Wisconsin Press, should serve as a useful reference to recent work in most of the areas of current interest.

In general, we are concerned in this article with aspects of Superconductivity and the two amazing liquids He^3 and He^4 which can appropriately be called Quantum Liquids.

SUPERCONDUCTIVITY

Theoretical developments.—The year 1957 has seen a great deal of activity concerned with the theory of superconductivity, and, at last, the problem can be considered largely solved. The start of this breakthrough was the suggestion first made by Frohlich (3) and by Bardeen (4) in 1950, that it is the interaction between the electrons and the lattice vibrations, when sufficiently strong, that is fundamentally responsible for the superconducting state. Although there was fairly convincing evidence of the correctness of this view, largely provided by the observed dependence of the energy involved on the mass of the atoms in the lattice—the isotope effect (5, 5a), mathematical difficulties prevented the solution of the interaction problem.

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[1] The survey of literature pertaining to this review was concluded February, 1958.

To help understand the ideas involved we note that in the simple theory of metals, the conduction electrons are considered as moving in the periodic field of the ions forming the crystal lattice. In a perfectly periodic field, the electrons behave as if "free" with an effective mass different from the ordinary mass. Deviations from strict periodicity, in particular arising from elastic vibrations of the lattice, modify the free motion of the electrons, and cause scattering, which leads to electrical and thermal resistance. In the quantum theory of conductivity the interaction between the electrons and these lattice vibrations is considered in terms of the emission and absorption of vibrational quanta or phonons. Effectively the electrons act as "sources" for the vibrational field in the sense of modern field theories. As in such theories there arises an effective interaction between electrons through mutual exchange of phonons. This effective interaction can be attractive and is the interaction responsible for the superconducting state. Now, the interaction between particles at rest is uniquely determined by their relative position, but for rapidly moving particles the interaction becomes velocity dependent because of retardation effects due to the finite velocity of the field. In the present case this velocity is that of sound. Since this is small compared with that of most electrons, the velocity dependence of the interaction is extreme, and it is best described in momentum space.

The difficulties of solving this many particle interaction problem are great. Indeed the large qualitative difference between the superconducting and normal states shows that ordinary perturbation theory is unlikely to be successful. Nevertheless, indications obtained with this method were very suggestive of the fact that the electron-phonon interaction is really the correct one. For example Frohlich (6) was able to solve the one dimensional case and showed that there is an energy gap in the excitation spectrum. Kuper (7) showed that this gap decreases with increasing temperature and vanishes at some temperature at which there is a second order thermodynamic transition back to the normal "one dimensional metal." A review of the state of the theory at this stage can be found in Bardeen's article in *Handbuch der Physik* (8).

The mathematical difficulties in the way of dealing with the electron lattice interaction held up progress for many years. Recently, however, Bardeen, Cooper & Schrieffer (9) succeeded in solving a somewhat simplified problem which, nevertheless, retains most of the essential features of the actual one. This solution, in which electrons are coupled in pairs, does indeed lead to most of the qualitative features expected (8), particularly the existence of an energy gap separating the lowest state of the system from any excited state, the energy gap being produced by a cooperative effect of the interaction and being temperature dependent, vanishing at the transition temperature. As had been expected on phenomenological grounds, increase of temperature from zero excites electrons across the energy gap and out of the cooperative distribution, thereby weakening the effect producing the gap so that eventually at a transition temperature, T_c, the gap goes to zero and the normal state is restored. Comparison of the results of this theory with experiment yields quite remarkable agreement, including even some of the finer

details. The fact should perhaps be emphasized that until recent developments, superconductivity was one of the very few remaining phenomena in the realm of atomic physics that had defied theoretical understanding.

In addition to the thermodynamic properties the theory is claimed also to lead to the unique magnetic property of the superconducting state, namely the Meissner effect. This proof has been questioned on a number of formal grounds by Buckingham (10), Schafroth (11) and others, particularly in question being the gauge invariance of the theory and the uniqueness of the operator used to represent the current density. Anderson (12) and Rickayzen (13) have also attempted to analyze the situation but the answer appears still in doubt.

A somewhat different and perhaps more rigorous theory has been developed by Bogoliubov (14) in Russia. In this theory the original Hamiltonian suggested by Frohlich (3), for which the current operator can be uniquely defined, is subjected to a canonical transformation which permits an approximate solution that indeed has the same features as the theory of Bardeen, *et al.* It is thought that this solution may resolve the difficulties in the proof of the Meissner effect. An interesting and quite differently based theoretical approach had earlier been advanced by Schafroth, Butler & Blatt (15) in Australia. They consider that the proved (16, 16a) superconductivity of the charged ideal Bose gas is the key to understanding the phenomenon, and have developed a statistical mechanical approach in which the interaction effectively binds electrons in pairs so that they behave somewhat like Bose particles. There may well be a connection between these two points of view, although such has not yet been established.

Experiments.—Parallel with this great activity of the theoreticians, the experimentalists have extracted new knowledge concerning several features of the phenomenon. More and more experimental evidence for the energy gap has been found from specific heat measurements [Corak, Goodman, Satterwaite and Wexler (17, 17a)], absorption and transmission of high-frequency microwave and infrared radiation and from ultrasonic attenuation measurements. The rapid increase in absorption for microwave frequencies for which the photon energy is greater than the energy gap has been observed in Sn and Al [Blevins, Gordy & Fairbank (18); Biondi, Garfunkel & McCoubrey (19); Forrester, Biondi & Garfunkel (20)]. Some interesting experiments on transmission through superconducting films, as thin as 20 atomic layers, by Glover & Tinkham (21) have revealed the same features and also illustrate again the striking fact that superconductivity still exists in such two dimensional specimens. What is perhaps a less indirect way of measuring the energy gap, is provided by ultrasonic attenuation experiments. Such experiments have been performed by MacKinnon (22), Mason & Bommel (23), Morse *et al.* (24, 24a), leading to results in substantial agreement with theory.

New intermetallic compounds between alkaline earths and noble metals have been discovered by Matthias & Corenzwit (25) at Bell Laboratories to add to the long list of new superconductors conjured out of the periodic table by Matthias and his co-workers. The empirical regularities in the ap-

pearance of superconductivity in the periodic system as pointed out by Matthias (26) is discussed in the light of the BCS theory (9) by Pines (27). Another surprising discovery was that a compound of two superconducting elements, zirconium and zinc, with approximate composition 1 Zr:2 Zn, becomes ferromagnetic below 35°K. [Matthias & Bozorth (28)].

Application to computer circuitry.—Although one might have considered superconductivity to be an example of a phenomenon without application outside a cryogenic laboratory, some exciting prospects for application to high speed computer circuitry are being developed. The cryotron, a switching element suggested by Buck (29), uses the magnetic field produced by a current in one wire to change another wire between the normal and superconducting state, thereby controlling the resistance in the second wire. The fact that a ring shaped superconductor can carry a persistent current and hence act as a memory element has been applied in the invention of other devices announced at the recent Low Temperature Physics Conference in Madison by Crittenden (30), Buckingham (31), and Crowe (32). These components have, in principle at least, the possibility of great improvement over conventional ones in simplicity, speed, and size. These advantages arise because of the combination of a number of properties, including: (a) the very small energy involved in the normal superconducting transition, only about 10^{-8} electron volts per atom, which is many orders of magnitude less than the equivalent for any room temperature phenomenon; (b) the unique electromagnetic behavior of a superconductor—zero electric resistance and perfect diamagnetism; (c) the fact that the transition can be induced by a magnetic field, a current, or by a temperature change; (d) the length parameter involved, about 10^{-5} cm., permitting almost microscopic size for components. These properties permit one to consider solid state computer units with a density of elements of 10^4 per cc. or more and with switching times down to 10^{-9} seconds, and we now wait for the results of further experimental work to see the extent to which these hopes can be achieved in practice.

QUANTUM LIQUIDS

Helium has a primary and unique position in the family of liquids. It is the only substance to exist as a liquid at 0°K. It exists as a liquid over a vastly larger range of reduced temperature (T/T_{crit}) than any other substance and both of the two stable isotopic species He^3 and He^4, following Fermi-Dirac and Bose-Einstein statistics respectively, are liquid in a temperature range where quantum effects might be expected to be all important. Thus in the higher temperature range, not too far from the critical temperature, 3.35°K. for He^3 and 5.2°K. for He^4, these liquids provide an opportunity for study of simple liquids with essentially classical properties. At lower temperatures quantum effects induce some dramatic properties, the liquids providing almost unique examples of degenerate quantum fluids. It is not surprising, then, that liquid helium research continues to dominate the low temperature literature. At the Wisconsin conference mentioned above, more than 60 papers were read on this subject. In this review we will attempt a brief summary of some recent advances in the understanding of liquid He^4

and a review of the status of the He³ problem. For more complete summaries of earlier work with bibliographies several excellent reviews are available [London (33); Wilks (34, 35); Daunt (36); Daunt & Smith (37); Dingle (38); Long & Meyer (39)].

Liquid He⁴

Background.—In order to place in proper perspective some recent experiments on liquid He⁴ it will be helpful to review certain well established facts about this liquid. (*a*) Helium does not solidify under its own vapor pressure but exists as a liquid at 0°K., its most ordered state; (*b*) at 2.17°K. the liquid undergoes a phase transition accompanied by a large lambda type specific heat anomaly; (*c*) above this lambda temperature the liquid (called helium I) is similar in most respects to other liquids; (*d*) below this lambda point the liquid (called helium II) has most curious transport properties (frictionless flow, creeping film, large heat conductivity, second sound, etc.).

The startling fact, that helium unlike all other substances is a liquid at the absolute zero of temperature, is a direct consequence of quantum theory. Classically, motion ceases at 0°K. but quantum mechanically, there always exists a zero-point motion. Because of its small mass this zero-point energy is large for He; furthermore, the van der Waals attractive forces are very small. Therefore, at 0°K. the minimum of the total energy, zero-point plus potential, is not achieved in the spatially ordered condition which minimizes the potential energy in ordinary solid crystals; rather it is achieved by a kind of momentum ordering in a liquid phase of large molar volume (27 cm.³) [London (33)].

The basis of a fundamental theoretical explanation of the lambda transition and the unique quantum behavior of HeII in terms of an analogy with condensation of an ideal Bose gas was made by F. London. The development of the two fluid concept and its explanation in terms of excitation theory is due to Tisza (40) and Landau (41 to 44). The principal features of the theory as it now appears were given by Landau in his famous 1941 paper (41). Parts of it have been extended and put on a much firmer basis by Feynman (45, 46, 47) and others, but the Landau picture is still essentially intact.

Nature of the excitations in HeII.—The first question the theory attempts to answer is what is the nature of the thermal motions in the liquid or what kind of excited states are possible in liquid HeII. Based on quantum hydrodynamic arguments now considered invalid, in spite of the success of their conclusions, Landau arrived at excitations of two kinds—phonons and rotons. The excitations of lowest energy were the phonons or quantized sound waves, whose energy E was related to the momentum p by the relation

$$E = cp \qquad\qquad 1.$$

where c is the velocity of sound. The rotons, separated from the ground state by an energy gap Δ, had energies given by

$$E = \Delta + p^2/2\mu \qquad\qquad 2.$$

where p is the momentum and μ the effective mass.

In order to obtain agreement with Peshov's second sound results he later revised the roton spectrum (43) to

$$E = \Delta + (p - p_0)^2/2\mu \qquad\qquad 3.$$

where p_0 is a constant. He then suggested that these excitations were basically similar and that the energy $E(p)$ was directly proportional to the momentum p for low energy excitations, but as the momentum increased the energy reached a maximum, then dropped to a minimum, Δ, and then rose again. Since only the states near $p=0$ and near the minimum of the energy momentum curve are excited in the low temperature range in which HeII exists the rest of the shape of the curve is not important in the calculation of the properties of the liquid. Hence, Landau assumed that only the phonon and roton excitations as defined by equations 1 and 3 need be considered.

The experimental data support rather well the Landau theory. At very low temperatures, below about 0.6°K., all the available evidence supports the assumption that phonons are the only mode of motion excited. The specific heat calculated for a Debye phonon spectrum is $C_v = 0.0207(\pm 0.0005)T^3$ joules/gm. deg. using the extrapolated sound velocity values of Atkins & Chase (48). This is in excellent agreement with the latest experimental value $C_s = 0.0204(\pm 0.0004)T^3$ joules/gm. deg. [Wiebes, Niels-Haklenberg & Kramers (49)]. These latest experimental measurements are about 10 per cent below the earlier values of Kramers, Wasscher & Gorter and remove the small discrepancy that existed previously between the Debye phonon calculated value and experiment. Further support for the phonon picture is given by the behavior of heat flow below 0.6°K. [Fairbank & Wilks (50)]. Heat conduction is accurately described by the formula of Casimir (51) for the thermal conductivity of a dielectric solid where the phonon excitations are scattered only by the boundaries of the specimen. Further evidence is seen in the coefficient of thermal expansion which appears to be positive below 0.6°K. in agreement with expectations if only sound waves are present [Atkins & Edwards (52)]. Finally the behavior of second sound in this temperature range is consistent with this picture [Gorter (53); de Klerk, Hudson & Pellam (54); Kramers (55); Osborne (56); King & Fairbank (57)].

What is the nature of the rotons? Landau (41) described them as some kind of rotation in the liquid. Feynman is more explicit. He derives and defends this excitation spectrum on a much sounder basis from first principles. The roton is pictured as an analogue to a smoke ring [Feynman & Cohen (47)]. The wave function representing the roton state can be described as a vortex ring of sufficiently small radius that only one atom can pass through the center. A slow drift of atoms returning for another passage takes place outside the ring.

From the excitation spectrum, equations 1 and 3, and the supposition that the excitations obey Bose statistics, the thermodynamic functions can be calculated. Therefore, the values of the roton spectrum parameters, Δ, p_0, and μ, can be adjusted to give the best fit to experimental thermodynamic data. Values of these parameters are given in Table I. The first

values were calculated by Landau (43), in 1947, to fit the specific heat and second sound data. They have been revised by de Klerk, Hudson & Pellam (54) to fit more recent values of second sound velocity down to 0.15°K. and again by Wiebes, Niels-Haklenberg & Kramers (49) to fit their latest values of specific heat below 0.7°K.

Feynman goes further than Landau in that he obtains a Landau type energy-momentum curve for the excitations from first principles by the substitution of a trial wave function into a variational principle for the energy. For the latest wave function Feynman & Cohen (47) find the values given in Table I. This curve should be considered as an upper limit to the true spectrum.

TABLE I

VALUES OF THE PARAMETERS OF THE ROTON EXCITATION SPECTRUM

Reference	Δ/k	$p_o/\hbar$	μ/m_{He}
Landau (1947)	9.6°K.	1.95 A^{-1}	0.77
Revised, de Klerk et al. (1954)	9.6	2.30	0.40
Revised, Wiebes et al. (1957)	8.8 (± 0.1)	1.96 ± 0.05	0.23 ± 0.1
Feynman & Cohen (1956)	11.5	1.85	0.20
Palevsky et al. (1957)	8.1 ± 0.4	1.95 ± 0.2	0.16 ± 0.02
Yarnell et al. (1958)	8.6 ± 0.2	1.93 ± 0.4	—

New evidence from neutron scattering.—Early in 1957, Cohen & Feynman (58) suggested that the energy-momentum curve for the excitations in helium could be measured directly by studying the energy distribution of very slow neutrons scattered inelastically from HeII below about 2°K. They point out that the most important scattering process is one in which the neutron produces or annihilates a single excitation. If the incident neutron beam is monochromatic the change in momentum and energy of the neutron in such a scattering process gives the energy and momentum of the excitation.

Successful experiments of this type have now been performed at Aktiebolaget Atomergi in Stockholm by Palevsky et al. (59), and at Los Alamos by Yarnell et al. (60). Similar work is also in progress at Chalk River, Canada by Henshaw. In place of the nonexistent monoenergetic neutrons, Palevsky et al. pass thermal neutrons through a polycrystalline Be filter, which results in a neutron spectrum characterized by a sharp rise in intensity at 3.96A, and falling off as $1/\lambda^5$ for longer wavelengths. Neutrons with this energy spectrum are directed at a helium target and the energy spectrum measured at a fixed scattering angle. For neutrons scattered from liquid HeII the energy spectrum of the scattered neutrons is similar in shape to that of the incident beam but the sharp cutoff is shifted to a lower energy value. The energy and momentum of the single excited roton in helium is then inferred. Yarnell et al. have proceeded in essentially the same manner with similar results. The energy-momentum curve can be traced out in the region of the roton spectrum by using filters with different Bragg cutoffs or by changing

the scattering angle. The excitation curve, qualitatively, is in remarkably good agreement with the Landau-Feynman theory, showing the minimum at $p = p_0$ and the maximum at smaller momentum. The Los Alamos measurements include points on both sides of this maximum. A straight line joining the origin and the first measured point on the energy momentum curve has a slope corresponding to $c = 240 \pm 20$ m/sec.. in excellent agreement with the measured velocity of sound [237 m./sec. (48)]. The maximum is symmetric and occurs at $p/\hbar = 1.10 \pm .04$ A^{-1} and $E(p) = 13.8 \pm .2°$K. The values of Δ, p_0 and μ deduced from the position and shape of the minimum are given in Table I. Yarnell *et al.* do not find the spectrum to be symmetric about the minimum, and do not calculate a value of μ. Additional experiments of this sort are planned to check on further details. However, there is little question of the basic correctness of the Landau-Feynman energy spectrum as a result of these beautiful direct measurements.

Fundamental nature of superfluid flow.—The fundamental nature of the motions possible in superfluid helium has been the object of many interesting experiments during the past year. In particular, types of flow experiments, such as that through very narrow channels, have shown over many years that helium II, flowing at velocities less than some critical value, flows without apparent friction [see for example Winkel & Wansink (61)]. Channels such as this act as "entropy filters" in which mass and momentum transfer takes place without energy or entropy transport. These phenomena are described in terms of the two fluid concept which picture the HeII as a mixture of superfluid and normal components, the latter being associated with the thermal excitations (rotons and phonons) of the liquid [Landau (41)]. Thus, in narrow channels only the superfluid flows, the normal fluid being left behind. Instead of the usual velocity field with which motion is described in ordinary fluids, the two-fluid theory requires two distinct velocity fields $\mathbf{v}_s$ and $\mathbf{v}_n$, one for each component of the liquid helium. The superfluid is restricted to irrotational motion.

The fundamental question arises: Does this apparently frictionless flow really correspond to irrotational motion of the superfluid or merely to an immeasureably small viscosity? In the first case $\nabla \times \mathbf{v}_s = 0$; in the second case $\nabla \times \mathbf{v}_s = $ const. (One is reminded here of the analogous distinction between a true superconductor in which $\mathbf{B} = \nabla \times \mathbf{A} = 0$, Meissner effect, and a perfect conductor in which $\mathbf{B} = \nabla \times \mathbf{A} = $ const.) This question is particularly important in that it concerns not only transport properties but also fundamental properties of thermodynamic equilibrium. That is, we can also pose the question: What is the equilibrium state for a volume of superfluid with angular momentum M? As is well known the equilibrium configuration for any liquid with nonzero viscosity, no matter how small, corresponds to that of a solid body. The value of the viscosity merely determines the rate at which this equilibrium is achieved. For this type of motion $\nabla \times \mathbf{v} = 2w$. What then happens to a liquid which can partake only in irrotational motion?

This question is discussed in *Superfluids* (33) in which is developed London's suggestion (62) that the angular momentum may be carried in

vortex sheets, i.e., surfaces of discontinuous velocity separating regions of irrotational flow. Onsager (63) suggested that this angular momentum is actually carried in vortex lines, and indeed such a solution turns out to have a lower energy than that in terms of vortex sheets. Feynman (46) independently developed this solution and discusses it in considerable detail. The intriguing feature emerges that the vorticity (or circulation) should be quantized.

$$\text{Circulation} = \oint \mathbf{v}_s \cdot d\mathbf{s} = nh/m$$

where the integral is around a path enclosing the vortex line, n is an integer and m is the mass of a helium atom.

An example of the fundamental difference between irrotational flow and that with very small viscosity is the lift on an airfoil. In the latter type of motion the lift on an unstalled airfoil is proportional to ρv^2 regardless of the actual value of the viscosity. In the former case of potential flow, however, the lift is zero. Craig & Pellam (64) have performed an ingenious experiment to measure the lift on an airfoil in a superfluid wind tunnel. They installed an entropy filter in the form of a semipermeable plug at each end of a tube through which helium is made to flow. Between the plugs the flow is characterized by $v_n = 0$ and $v_s \neq 0$; they thereby eliminate any effects due to normal component flow and obtain their superfluid wind tunnel. Using fly wings, thin strips of mica, etc. for air foils they succeeded in obtaining sufficient sensitivity for the experiment. They found that for velocities less than a critical value v_c of a few mm./sec. the lift was indeed zero. For higher velocities the lift was proportional to $v_s(v_s - v_c)$. Thus, this experiment does support the view that superfluid helium at sufficiently small velocities is restricted to irrotational flow, and that it cannot be described in terms of zero viscosity alone. Another experiment bearing on this point is being attempted by Reynolds, Good & Schultis (65). They measure the hydrodynamic effective mass of a cylinder moving through liquid HeII.

Let us return now to the question of the equilibrium state for a volume of superfluid in steady rotation with angular momentum M. An experiment now in progress by Vinen (66) at Cambridge appears to give confirmation to the quantization of circulation in rotating superfluid helium and indication of a persistent superfluid current existing for some time after the rotating vessel has been stopped. In this apparatus helium is contained between two concentric cylinders (radii a and b; $b > a$) rotating about their common axis. By measuring the modes of transverse oscillation of the wire, generated by passing a current through the wire in a transverse magnetic field, the superfluid circulation around the wire can be measured to within 2 to 3 per cent of a single quantum of circulation h/m. A typical experiment consists of starting the cavity in rotation above the lambda point until the equilibrium solid like rotation is achieved, cooling slowly to 1.3°K., measuring the circulation, stopping the rotation then measuring the circulation as a function of time.

There are certain complications but the results appear to show that for angular velocities a little greater than

$$w_o = \frac{\hbar}{m} \frac{\ln b/a}{b^2 - a^2}$$

(about 7.5 r.p.h.) the circulation is of order h/m around the wire in agreement with the expectation of theory of Onsager and Feynman. When the rotation is stopped the superfluid circulation settles to a value h/m and remains steady for as long as $1\frac{1}{2}$ hours, demonstrating a metastable persistent superfluid current.

The existence of the Onsager-Feynman vortex lines in rotating liquid helium is supported by further experiments of Hall & Vinen (67) in which they investigate the propagation of second sound in a uniformly rotating vessel filled with liquid helium II. No change in the velocity of second sound is found, but the attenuation is found to be proportional to the angular velocity of rotation and much larger for directions of propagation that lie in a plane normal to the axis of rotation than for the axial direction. They interpret this as due to a mutual friction between normal and superfluid flow due to collisions between normal fluid excitations and the vortex lines. A somewhat similar experiment by Blakewood, Wheeler & Lane (68) showed greater attenuation probably due to the different geometry of this apparatus which produced more turbulence in the liquid.

Vinen (69) explores this idea further in some experiments on the heat conduction through helium II in large channels (cross section $\sim 2 \times 6$ mm.). He finds that steady heat flow leads to an attenuation of second sound, propagated across the heat current. Phenomenologically, this can be described by a mutual friction between the two fluids of the Gorter-Mellink type (70), proportional to $\mathbf{v}_s - \mathbf{v}_n$ and the time average of the relative velocity. Vinen suggests that the Gorter-Mellink force is associated with turbulence in the superfluid and that this turbulence takes the form of a tangled mass of quantized vortex lines.

A rotation experiment in progress by Walmsley & Lane (71) raises some puzzling questions. They attempt to measure the angular momentum of a rotating cylindrical vessel of helium II by suddenly stopping the steady state rotation and observing the subsequent torque as a function of time on a fiber supporting the vessel. Above the lambda point the angular momentum M of the helium is found to be that of a rigid rotating cylinder, M_o. At lower temperatures M/M_o is less than 1, approaching a value of ρ_n/ρ at low speeds of less than 1 r.p.m.

It is not yet clear how the details of this and some other experiments, for which space does not permit discussion, can be interpreted on the vortex line model. It is certain that no crystal clear picture of the fundamental character of superfluid flow and rotation has yet been reached. However, it can perhaps be said that the evidence supports irrotational flow at low velocities and is consistent in part with the existence of the Onsager-Feynman vortex line description of rotating motion. How turbulence sets in is not clear.

Nature of the lambda transition.—Some recent experiments have thrown

new light on the details of the lambda transition itself. Using a carefully designed calorimeter to insure the extreme degree of thermal equilibrium required, Fairbank, Buckingham & Kellers (72) have measured the specific heats of liquid helium under its saturated vapor pressure to within a few microdegrees of the transition. Equilibrium was achieved by enclosing 0.06 gm. of helium in a copper container of about 200 gm. with fins arranged so the helium was everywhere within a few thousandths of an inch of a copper surface. The results obtained showed that the specific heat has a logarithmic singularity at the lambda point rather than having merely a discontinuity as had usually been supposed. Meanwhile Hill & Lounasmaa (73) had obtained new accurate specific heat data over a wide temperature range up to the critical point and combining all these results together with those of Wiebes et al. (49), mentioned earlier, enables one to obtain the following empirical expression for the specific heat in joule/gm. deg.:

$$C_{sat} = 0.0204T^3 + 3.33e^{-6.7/T} \ln \frac{10}{T - T_\lambda} - 5.6\Delta$$

where $\Delta = 0$ for $T < T_\lambda$, $\Delta = 1$ for $T > T_\lambda$. This expression describes well the data up to about 2.5°K. and to within 10^{-6} deg. of the transition.

Thermodynamic considerations suggest that the above results implies that the density of the liquid has an infinite slope at the lambda point and a maximum at a slightly higher temperature, and a recent measurement of this quantity by Edwards (74) seems consistent with this view. It is interesting to note that this transition does not fit into the Ehrenfest classification of thermodynamic transitions, although it had usually been supposed previously to be of second order (C_p finite and discontinuous). Consideration of the lambda type transitions associated with many other physical phenomena of the cooperative type (such as magnetic, rotational and order-disorder transitions) suggests that these also have logarithmically infinite rather than discontinuous specific heats. It is also interesting to note that the only exact solution in statistical mechanics for a cooperative transition is that first found by Onsager (75) for the two dimensional Ising problem and that this has, in fact, just this logarithmic behavior.

He³

A Fermi-Dirac liquid.—As pointed out earlier, just as He⁴ with zero spin represents the only Bose-Einstein system in nature which remains liquid down to the absolute zero of temperature, so He³ with nuclear spin $\frac{1}{2}$ represents the only liquid system that obeys Fermi-Dirac statistics and does not freeze under its own vapor pressure at any temperature. It is of particular interest, therefore, to compare the behavior of these two systems as the absolute zero, or state of perfect order, is approached.

He³ occurs in only one part in 10^7 in well helium and one part in 10^6 in atmospheric helium (76). Because of this very small abundance, experiments on pure liquid He³ were not possible until He³, formed from decaying H³, was released in small quantities by the Atomic Energy Commission in 1948, and in larger quantities since 1952. Since that time research on He³ has in-

creased at such a rate that a four day international symposium was held in August, 1957, at Ohio State University devoted entirely to the subject of He^3 and He^3-He^4 solutions.

Not only are experiments on He^3 interesting for their own sake, but also for the light they throw on the theory of He^4 and in particular on the role of Bose-Einstein statistics in the theory of the superfluid state. If Bose-Einstein statistics are essential for the superfluid state, then He^3 would not be expected to be a superfluid at any temperature. Instead it would be expected to undergo ordering characteristic of a Fermi-Dirac system.

First let us examine the evidence on whether or not He^3 is a superfluid at any temperature. In their early viscosity measurements Osborne, Weinstock & Abraham (77) found no superflow down to 1.05°K. Daunt & Heer (78) extended this limit to 0.25°K. in measurements designed to detect a creeping film. Recent thermal conductivity measurements show no abnormal heat flow in liquid He^3 down to below 0.2°K. [Lee & Fairbank (79)], and the viscosity of the liquid continues to rise with decreasing temperature down to 0.35°K., indicating no superfluidity [Zinoveiva (80)]. This evidence seems to give further weight to the importance of Bose-Einstein statistics in the superfluidity of He^4. There has been considerable theoretical speculation on whether or not He^3 can become superfluid at sufficiently low temperatures. Landau (81), Houston & Rorschach (82), de Boer (83), and Rice (84) suggest this possibility. Mott (85), Toda & Ishihara (86), London (33) Feynman, (45, 46, 87), Penrose & Onsager (88), and Buckingham (89) are inclined to rule out superfluidity in He^3 at any temperature. It remains an interesting experiment to check this point to the lowest possible temperature.

Next, let us examine the type of ordering He^3 does exhibit and its relationship to the Fermi-Dirac statistics. At the absolute zero the nuclear spins of the He^3 molecules must be ordered. In the absence of statistical or quantum mechanical exchange effects, the nuclei would be expected to become aligned at a temperature of approximately 10^{-7} °K. due to the magnetic dipole-dipole interaction between nuclei. However, the spins of an ideal Fermi-Dirac gas, of the same spin, density, and atomic mass as liquid He^3 would begin to become antiparallel aligned at temperatures of the order of 5°K., the Fermi temperature for such a system. Since the particles thus aligned could not contribute to the magnetic susceptibility, this model would predict the nuclear magnetic susceptibility to deviate from the classical $1/T$ Curie law below 5°K. and finally to become temperature independent as the absolute zero is approached. Similarly the specific heat for He^3 on an ideal Fermi-Dirac gas model would become linear with temperature below about 0.4°K. For an ideal Fermi-Dirac gas model the viscosity would vary as $T^{1/2}$ at higher temperatures and as $1/T^2$ at temperatures well below the Fermi temperature. The low temperature thermal conductivity, on an ideal Fermi-Dirac gas model, would vary as $1/T$.

Measurements on the transport properties do not give much support to this ideal Fermi-Dirac gas model in the temperature range, above .2 to .3°K. The viscosity measurements do not show the T^{-2} dependence [Weinstock, Osborne & Abraham (90); Taylor & Dash (91); Zinovieva (80)]. Above

1°K., Taylor & Dash (91) fit the viscosity data to an empirical $T^{-0.38}$ power law. At lower temperatures the viscosity rises more steeply with falling temperature but does not reach a T^{-2} dependence down to 0.35°K. according to the results of Zinovieva (80). The thermal conductivity gradually rises from a value of about 0.6 watt/cm.°K. at 0.2°K. to about 1.9 at 2.7°K. giving no indication yet of a T^{-1} dependence [Lee & Fairbank (79); Challis & Wilks (92)]. It is possible that both the thermal conductivity and viscosity will show the characteristic temperature dependence of the ideal Fermi gas at sufficiently low temperatures.

The specific heat of liquid He³ has been measured by Abraham, Osborne & Weinstock (93), Roberts & Sydoriak (94), de Vries & Daunt (95), and recently by Brewer, et al. (96). The earlier work down to 0.23°K. showed no indication of the linear dependence but the latest measurements which go down to 0.1°K. show a linear dependence of specific heat on temperature, starting slightly below 0.15°K. and extrapolating to 0°K., with a slope of 3.75 cal./mole deg. This slope is 1.87 times that predicted for the ideal Fermi gas.

Fairbank, Ard & Walters (97, 97a, 97b) have measured the susceptibility by nuclear resonance techniques and find that the susceptibility falls below the classical Curie value, becoming independent of temperature at sufficiently low temperature, but with a value 11 times larger than that expected from an ideal gas model.

From these experiments it appears that the nuclear ordering expected of an ideal Fermi-Dirac gas is taking place in liquid He³, but in a manner very different from the ideal gas model. The slope of specific heat at the lowest temperature is equal to 1.87 times that of an ideal gas model, and the temperature independent susceptibility at the lowest temperatures is 11 times greater than for the ideal gas model.

Several theories have been put forward to explain the specific heat and susceptibility of He³. Prigogine & Philippot (98, 98a), Rice (99), Price (100), Temperley (101), and de Boer (83) have applied the liquid cell model to He³ in an attempt to explain the specific heat and the susceptibility. Houston & Rorschach (82) have considered wave function overlap of the He³ wave functions to lead to a motion of the nuclei through a periodic potential field. Goldstein (102), Yomosa (103), Lee, Huang & Yang (104), Kikuchi (105), Nanda & Trikha (106), Mikura (107), Bhagat (108), and Brueckner & Gammel (109), have considered a modified ideal gas model in which the interaction between the molecules are taken into account. Buckingham (110) has pointed out that at low temperatures the difference in the relationship of the susceptibility to that of an ideal gas, and the specific heat to that of an ideal gas, implies the existence of strong spin dependent exchange forces tending toward parallel alignment of the spins which affect strongly the susceptibility, but not the specific heat. Brueckner has presented a theory, based on the adiabatic transformation of an ideal gas at the absolute zero making use of trial wave functions and the Los Alamos computer, which gives quantitatively these two types of aligning tendencies and predicts a low temperature value of both the susceptibility and the specific heat in agreement with experiment.

The susceptibility at the lowest temperatures measured has become independent of temperature, and the specific heat is linear in temperature. It appears doubtful if these two quantities will yield any different information if measured to lower temperatures. The transport phenomena, however, might exhibit very revealing properties of the degenerate Fermi system if carried to temperatures of the order of 0.01°K.

The question of how pressure affects the properties of liquid He³, especially at very low temperatures is an interesting one. From nuclear susceptibility measurements it is found that the nuclear spin ordering is pushed to lower temperatures with increasing pressures [Walters & Fairbank (97)]. This would suggest, since the disorder is mostly in the spin system at temperatures below about 0.5°K., that the entropy increases with pressure at these temperatures. The Gibb's relation,

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T,$$

would require a negative expansion coefficient, and the density would have to have a maximum at some temperature below 1°K. since the measurements of Edeskuty & Sherman (111) show a decreasing density with increasing temperature above 1°K. In the heat flow measurements such a maximum in the neighborhood of 0.5°K. was inferred in order to explain the heat convection properties of the liquid [Lee & Fairbank (79)]. Other evidence for such behavior was discussed at the Ohio State Conference by Abraham, Osborne & Weinstock (112) and by Daunt (113).

Solid He³.—In 1951, Pomeranchuk (114) suggested that the spins in liquid He³ would become ordered at 5°K., but that the spins in solid He³ would remain unaligned until 10^{-7}°K. As a consequence there would be a minimum in the melting pressure curve below which the entropy of the solid, due to its greater spin disorder, would be greater than the entropy of the liquid. If this speculation were correct, temperatures of the order of 10^{-7}°K. could be reached by adiabatic compression of liquid He³ from the liquid to the solid phase. Weinstock, Abraham & Osborne (115) demonstrated that the melting curve for He³ is either independent of temperature below 0.35°K. or rising with decreasing temperature. The latter behavior would require the entropy to be larger in the solid than in the liquid.

Measurements of the nuclear susceptibility of He³ have been extended into the solid phase by Walters & Fairbank (116, 116a). It is found that the nuclear spin ordering occurs in the solid at a slightly lower temperature than in the liquid near the melting curve. However, the ordering begins about 0.2 rather than at 10^{-7}°K. and, therefore, a large temperature drop on adiabatic solidification would not be expected. The above authors did, indeed, find some heating on melting below 0.4°K., supporting the belief that the entropy of the solid exceeds that of the liquid below this temperature and that there is a minimum in the melting pressure curve.

A recent development of great interest is the discovery of a solid-solid phase transition in He³ [Mills & Grilly (117)]. The melting curve (118) has been accurately measured and also the change in volume on melting to very

high pressures (114). From the latter measurements there are found two solid phases of different molar volume at temperature below 3.15°K. and pressure of 141 kg./cm.². The phase transition pressure decreases with decreasing temperature and has been measured down to 1.8°K.

It is interesting to speculate on the magnetic properties of these two solid phases, especially in view of some recent nuclear susceptibility measurements of Fairbank & Walters (116). They observed that under certain conditions (not yet clearly understood) an apparent parallel alignment of the nuclear spins in solid He³ occurs below 0.2°K. instead of the usual antiparallel alignment. That is, the nuclear susceptibility rises above the Curie value rather than dropping below it. Buckingham (110) has pointed out that alignment in solid He³ could be either parallel or antiparallel, depending on the sign of the exchange energy and the configuration of neighboring atoms. Can it be that two phases of the solid exist in which the stable configuration of the nuclear spins is that of antiparallel alignment for one and parallel alignment for the other? Preliminary measurements of the specific heat in the solid phase have also shown an anomaly at 0.12°K. [Brewer *et al.* (96)]. Clearly, further study of solid He³ at low temperatures is called for.

This review of He³ is by no means inclusive of all the recent work and omits mention of much of the earlier work. Furthermore the whole subject of He³-He⁴ mixtures has been omitted. The reader is referred to excellent earlier review articles by Daunt (36), Hammel (119), Beenakker & Taconis (120), Long & Meyer (39), and to the full proceedings of the Ohio State Symposium on Liquid and Solid He³ (1957).

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SOLUTIONS OF ELECTROLYTES[1]

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The author of this review is admittedly prejudiced in favor of electrolytic conductance. For this reason he considers the recent theoretical extension of the interionic attraction theory of conductance of outstanding importance and will discuss it in some detail. In the space remaining he will guide the reader to some of the more significant aspects of experimental work on electrolytes which have appeared in the recent literature. Since the literature in the Russian language seems less readily available to American readers than it should be, he will include it in a separate section of this review for convenience.

ELECTROLYTIC CONDUCTANCE

Onsager (1) stated long ago that terms of order $c \ln c$ in addition to terms of order c and higher are theoretically necessary to describe the departure of the actual conductance curve for a strong electrolyte from its limiting tangent. Shedlovsky, Brown & MacInnes (2) proposed an empirical conductance equation of the form

$$\Lambda_0 = (\Lambda + \beta\sqrt{c})/(1 - \alpha\sqrt{c}) - Bc + Dc \log c \qquad \text{(I)}$$

in which α and β are the Onsager constants. It was recently pointed out, however (3), that an expansion of the form of (I) was theoretically valid only at concentrations so small that deviations from the limiting tangent were only slightly larger than the experimental uncertainty in the data; the B and D terms of (I) represent the limiting form of a transcendental function

$$\text{Tr}(\kappa a) = e\kappa a \int_{\kappa a}^{\infty} e^{-t} dt/t$$

which appears in the higher terms. In the practical working range of concentrations, the first few terms of the series do not provide a satisfactory approximation. Fuoss & Onsager (4) published a preliminary statement of the explicit theoretical conductance equation which for 1:1 salts in water reproduces experimental data up to about 0.1 N, and have also presented the details of the derivation (5).

The original Debye-Hückel-Onsager treatment of the conductance problem considered point charges in the ionic model. Introduction of boundary conditions for the radius $r = a$ immediately leads to terms of order c, as might be expected. In 1932, Onsager & Fuoss (6) derived a general equation of continuity for mixtures of electrolytes. Before integration they dropped terms of higher-order than linear in the charge of the reference ion, ϵ_j. These neglected terms give rise to terms of order c and also to transcendental terms in

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[1] The survey of literature pertaining to this review was concluded February, 1958.

the conductance equation. Therefore use of a spherical model for the ions requires that the higher terms in the differential equation be retained. In their approach to the problem Fuoss and Onsager used the following procedure. First, they adjusted the solution of the equation of continuity, correct to terms of order ϵ_j, to the boundary conditions for $r=a$ rather than for $r=0$. These conditions correspond to nonsingular potential and field at infinite values of r, continuity of field at $r=a$, and impenetrability of two ions, since the normal component of relative velocity must vanish at $r=a$. Second, they inserted the first-order solution in the higher-order (inhomogeneous) terms of the equation of continuity, which they then resolved as a perturbation problem. The result is an explicit form of the relaxation term in the conductance equation, valid up to terms of order $c^{3/2}$, which combined with the 1932 (6) calculation of the electrophoresis term, gives a conductance equation which can be written in compressed form as

$$\Lambda = \Lambda_0 - (\alpha'\Lambda_0 + \beta')\sqrt{c} \tag{II}$$

where α' and β' are now functions of concentration of the general pattern

$$\alpha' = \alpha[1 + P(\kappa a) \, \text{Tr} \, (\kappa a)]$$

where $P(\kappa a)$ indicates polynomial expressions and Tr (κa) transcendentals.

In its limiting form (II) leads to (5)

$$\Lambda = \Lambda_0 - (\alpha\Lambda_0 + \beta)\sqrt{c} + Dc \log c + (J_1 c - J_2 c^{3/2})(1 - \alpha\sqrt{c}) \tag{III}$$

in which the constants J_1 and J_2 are explicit functions of ion size, (a), Λ_0, and of the properties of the solvent; the constant D is, however, independent of (a). The last two terms in (III) can be approximated by $cB(\kappa a)$ up to concentrations of about 0.01 N. The authors give numerical tables for computing $B(\kappa a)$ and describe a method for obtaining the two emprical parameters, Λ_0 and a, from conductance data.

The new conductance equation contains only two arbitrary constants, Λ_0, which has definite physical significance, and the ion size, a. This latter is a required parameter of molecular dimensions to include all the mathematical and physical approximations which are necessary in order to achieve a solution of the conductance problem in closed form. Thus far, the equation has been tested against experimental data for the cases of lithium, sodium, and potassium halides in water (5,6); the ion sizes found are in the range of values which are obtained in the computation of activity coefficients. The limiting equivalent conductances agree within a few hundredths of a unit with the values obtained by the empirical Λ' extrapolation method (7). Fuoss and Onsager used their equation over a concentration range below 0.1 N and imply that it should not be used at higher concentrations. Since their result depends on explicit use of the Debye-Hückel potential

$$\psi_j{}^\circ = e^{\kappa a - \kappa r}\epsilon_j/rD(1 + \kappa a)$$

and since the use of κ in turn implies a continuous distribution of charge, this upper limit seems reasonable. For aqueous solutions of ordinary 1:1 salts,

κa is numerically about the same as $c^{1/2}$; hence $c = 0.1$ corresponds to κa of about 0.3, which corresponds to approximately three ionic diameters. The concept of an ion atmosphere certainly must lose physical significance when average interionic distances reach this order of dimension.

The new conductance equation now provides theoretical explanation of the long-known experimental fact that the conductance curve for normal strong electrolytes in water approaches its limiting tangent from above; long-range interionic forces can give only positive deviations and any observed negative deviations must therefore find their explanation in short-range effects such as ion association. Although it makes relatively little difference whether one uses the limiting Onsager tangent or the new equation which shows positive deviations from this tangent, as a criterion for analyzing conductance curves of very weak electrolytes, this is not the case for "intermediate" electrolytes. Here, the new equation should be used in combination with the mass action law. Fuoss (8) has done so and shown how the values for Λ_0, (a), and the ionic association constant, A, can be obtained by graphical means from conductance data on low concentrations of moderately weak electrolytes, even of those approaching $A = 1$. He points out, however, that a viscosity correction is required if one of the ionic species is large compared to the solvent molecules.

Fuoss & Kraus (9) have applied this treatment of conductance data to several salts in dioxane-water mixtures with gratifying results. For example, they find that the value of a (4Å) remains constant within a few per cent for sodium bromate solutions as the composition of the solvent was varied from pure water to 55 per cent dioxane, dielectric constant, 31.5.

Conductance and transference data.—Conductance measurements are not difficult to make if one is not interested in work of the highest precision. However, unless the data are of high precision they have negligible theoretical interest. Nevertheless, the following papers should warrant the attention of workers interested in the field.

In water, Campbell, Debus & Kartzmark (10) have reported measurements on lithium nitrate at 25° and 110°C.; Chambers, Stokes & Stokes (11) on concentrated sodium chloride and potassium chloride at 25°C.; Ukihashi (12, 13, 14, 15) on sodium silicate at several temperatures. Spiro (16) has measured the transference numbers of iodic acid solutions at 25°C., and Breck (17) that of cadmium and thallous solutions. Turning to nonaqueous solvents of high dielectric constant, Dawson, Sears & co-workers reported on transference numbers of potassium chloride in formamide at 25°C. (18); on solutions of sodium and potassium halides in N-methylpropionamide and N-methylbutyramide from 30° to 60° C. (19); on some limiting ionic conductances in N-methylacetamide at 40°C. (20); and on 1:1 electrolytes in N-dimethylacetamide at 25°C. (21, 22).

Especially noteworthy measurements in alcohols are those of Graham, Kell & Gordon on the conductance of lithium, sodium, and of potassium chlorides in ethanol at 25°C. (23), those of Graham & Gordon on the trans-

ference numbers of lithium and sodium chloride in ethanol at 25°C. (24), and those of Brody & Fuoss (25) on the conductance of several Bolaform electrolytes (those containing ions in which at least two charged sites are joined by a chain of netural atoms) in methanol and in ethanol. Also, Campbell & Debus (26) have reported conductance studies on lithium nitrate solutions in ethanol and in ethanol-water mixtures at 25°C.

Among the English studies on conductance in nonaqueous solvents the following are of interest: quaternary ammonium and amine picrates in acetonitrile by French & Muggleton (27); alkali iodides and salicylates in ethyl methyl ketone and acetophenone by Hughes (28); silver salts in nonaqueous and mixed solvents by Griffiths & Pearce (29).

For conductance studies in concentrated sulfuric acid, in liquid sulfur dioxide, and in anhydrous hydrogen fluoride bold potential workers in these fields are referred to the papers by Schwab (30), Ilse & Hartmann (31), and Kilpatrick & Lewis (32), respectively.

THERMODYNAMIC PROPERTIES

Data relative to the thermodynamic properties of solutions continue to accumulate. These, of course, include a large number of electromotive force measurements on cells with, and without, transference, studies based on electrometric titrations, on conductance, and a few recent studies which have used isopiestic or spectrophotometric methods. Since the theoretical considerations underlying these methods are well-known and not really important advances have been reported in the past year, they will not be discussed in this review. The recent emf. studies include work on solutions in aqueous, nonaqueous, and mixed solvents from which activity coefficients and ionization constants were obtained.

Electrodes.—As far as electrode technique is concerned, Hamer & Craig (33) have described a reproducible, stable silver-silver oxide electrode for cells of the type: Hg, HgO:NaOH soln.:Ag$_2$O, Ag. For this cell they find $\Delta F = -11254$ cal.; $\Delta S = -9.12$ e.u.; and $E° = -0.342$ v., the standard potential of the Ag$_2$O, Ag electrode at 25°C. Taniguchi & Janz (34) described the preparation of a very satisfactory thermal electrolytic silver-silver chloride electrode for work of high precision. The standard potentials of silver-silver halide electrodes have been studied in ethanol solutions of hydrogen halides by Mukherjee (35). He finds that ΔF for the transport of these acids from ethanol to water increases with the anionic crystallographic size. Mukherjee has also studied the Ag, AgCl electrode in formic acid and acetic acid as solvents (36). The standard potentials, $E°(Hg_2^{++}, Hg)$ and $E°(Hg^{++}, Hg_2^{++}, Pt)$ have been reported to be 0.7925 v. and 0.9075 v., respectively, at 25° by Hietanen & Sillen (37) from measurements in nitrate and perchlorate solutions.

Activity coefficients.—Activity coefficients for dilute aqueous nitric and perchloric acids calculated from the emf. of glass electrode cells with transference and transference number measurements are reported by Covington

& Prue (38). They also find agreement between their values for HCl at 0°C. and results obtained from cells without transference.

In many aqueous solutions containing two electrolytes with a common ion the log activity coefficient of one solute at constant total ionic strength is a linear function of the ionic strength of the second solute. This has come to be known as Harned's rule (39, 40). Argersinger & Mohilner (41) find that for such three component aqueous systems, in which one solute obeys Harned's rule, the activity coefficient for the second solute and the osmotic coefficient for the solution may be directly computed. They appy such computations to mixtures of HCl with $BaCl_2$, $SrCl_2$, $AlCl_3$, and $CeCl_3$. The influence of second electrolytes on activity coefficients in aqueous solutions were experimentally studied by several authors: benzoic acid with KCNS, NaCNS, and KPF_6 (42), zinc sulfate with $MgSO_4$ and Na_2SO_4 (43), sulfuric acid with Ag_2SO_4 (44).

Using the isopiestic method, Brubaker (45, 46) has determined the activity coefficients for several electrolytes of high-charge in water: potassium octacyanomolybdate, tris-ethylene-diamine platinum chloride, tris-ethylene-diamine platinum perchlorate, and tris-ethylene diamine cobalt chloride. He finds that the data are in accord with the Debye-Hückel equation up to concentrations of 0.1 molar.

Ionic association.—Electromotive force studies of complex ion formations were reported for mercury in sulfate solutions (47), ferric thiocyanates (48), and silver iodides (49). Diebel & Swinehart (50) have carried out emf. measurements on cells without liquid junctions for aqueous orthanilic acid from 0° to 50°C. from which they computed the ionization constants. They found the standard entropy, $\Delta S° = -3.3$ e.u., which is considerably larger than for sulfanilic or metanilic acids.

Using electrometric titrations Peltier & Kerdavid (51) have determined the pK values for a number of parasubstituted 3-methylbenzoic acids, including H, NO_2, Cl, Br, OH, OMe and NH_2 as the substituents. These values range from 3.65 for the NO_2 group to 4.81 for NH_2. The values for *para*-aminobenzoic acid, as well as the methyl, ethyl, propyl and butyl esters have been found, by spectrophotometric measurements (52), to be about 2.5 at 25°C. For 2,4-, 2,6- and 3,4-dichlorobenzoic acids the pK's are 2.76, 1.82 and 3.64, respectively, while for 2,6-dimethoxybenzoic acid pK = 3.44, according to Davis & Hetzer (53) who used spectrometric (54) and glass electrode titrations in their work.

Calculations from emf. data at different temperatures of the acid and base dissociation constants, as well as the corresponding enthalpy, free energy and entropy changes for methionine (55) are not very different from earlier values found for glycine, valine and serine. The acid dissociation constants and the related thermodynamic quantities for piperidinium ion have been determined from careful emf. studies from 0° to 50°C. by Bates & Bower (56). For readers especially interested in spectrophotometric studies of ion association the following papers deserve mention. Potassium ferro-

and ferri-cyanide with thallous chloride (57); uranyl salts in water and 2,4-dinitrophenol, chloracetic acid, propionic acid in 20 per cent aqueous ethanol (58); heats and entropies of ferric ion hydrolysis (59); and ionic association of lead nitrate, cupric sulfate and cobalt hexamine sulfate in water (60). The results in this last paper are compared with those obtained from conductance.

Sivaramakrishnan (61) has carried out magneto optic rotation and optical dispersion measurements on a number of acids and salts at various concentrations from which he has obtained specific Verdet constants, molecular magnetic rotativity, optical dispersity and magneto optic "anomaly" factors by extrapolation to infinite dilution. The ions considered were Li^+, K^+, Na^+, NH_4^+, Ca^{++}, Sr^{++}, Ba^{++}, Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, $SO_4^=$, $PO_4^≡$.

The formation of thallous ion-univalent anion pairs was studied by Nair & Nancollas (62) by solubility and conductance determination at several temperatures. The anions include OH^-, Cl^-, Br^-, NO_3^-, N_3^-, CNS^-. They found a linear relationship between the entropy of complex formation and the reciprocal of the combined ionic radii, but the values for N_3^- and CNS^- fell somewhat lower. A linear variation of pK with $1/T$ was observed for glycylglycine and for diglycylglycine which were found to behave as normal zwitterions by Kilpi (63) in studies at various concentrations of added potassium chloride from 15° to 35°C.

It is encouraging to find an increasing number of papers on work in non-aqueous and mixed solvents. Here, the behavior of ions tends to reveal their peculiar individualities more clearly, and the challenging problem of ion-solvent interactions in addition to those posed by interionic effects promise to yield to theoretical analysis as reliable data accumulate in this field. Taniguchi & Janz (64) have made a careful study of hydrogen chloride in ethanol using cells without liquid junctions. They find the standard potential in anhydrous ethanol for the silver-silver chloride electrode at 25°C., $E°$ $= -0.08138$ volt and the activity coefficient of HCl at 0.1 M to be 0.490. In water it is 0.904.

Sodium, potassium, and magnesium thiosulfates appear to be markedly associated in 50 per cent ethanol as revealed by shifts in the $S_2O_3^=$ absorption spectrum at about 250 mμ (65).

Izmaïlov & Ivanova (66) have investigated sodium and potassium halides in methanol solutions with the help of dropping amalgam electrodes under an atmosphere of hydrogen and silver-silver halide electrodes. They find the standard potentials for the latter at 25°C. to be 0.0101, 0.1328 and 0.2785 volts respectively for the chloride, bromide and iodide electrodes. In another publication (67) Izmaïlov summarizes earlier work and extends it in an attempt to correlate pK values with the solvent. He proposes the relation

$$pK = 2 \log \gamma_0(\text{ions}) - \log \gamma_0(\text{molecules})$$

in which γ_0 indicates activity coefficients at infinite dilution referred to a standard state in a single solvent.

In ethyl methyl ketone-water mixtures data have been obtained for HCl with the cell: $H_2(Pt):HCl:AgCl$, Ag by Feakins & French (68). An attempt

to extend the work to triethylene glycol-water systems failed because of the apparent failure of the AgCl, Ag electrodes in these mixtures.

Cells with the glass electrode have been used successfully by Grunwald & co-workers for hydrogen, sodium, and potassium chlorides in 70 per cent dioxane, 30 per cent water (69) and for carboxylic acids and their sodium and potassium salts in the same solvent (70). A former study of the dissociation of acetic acid in methanol-water mixtures with glass electrode cells (71) appeared to give K values not in accord with those found from conductance measurements (72). It is gratifying to report here that the discrepancy was not real but rested on an ambiguity of what was meant by volume composition of the solvent. The agreement between the results of the two quite different methods is actually well within the experimental error.

Returning to hydrogen chloride cells, measurements have been reported in acetone-water mixtures (73) and in pyridine (74). The ionization of pyrone acids which have been studied by conductance in water (75) promises to receive experimental attention in other solvents. Conductance has been used to determine the ionization of sodium trimethylboron in tetrahyfuran (76). The values are $K = 4.3 \times 10^{-5}$ at 20°C. and 2.2×10^{-5} at 35°C.

Ion-solvent effects.—The dependence of charge and ionic radius on ionic entropies in water, which has been investigated by Laidler (77), has also been correlated with partial molal volumes (78, 79). From partition solubility studies of $KClO_4$, $KReO_4$, $RbClO_4$, $CsClO_4$, $CsReO_4$ in nitromethane (water), and the solubility of nitromethane in aqueous $HClO_4$, $LiCl$, $LiClO_4$, $NaCl$, $NaClO_4$, KCl, and $CsCl$, Haugen & Friedman (80) have calculated the free energy of transfer of ions from water to water saturated with nitromethane.

Data on the viscosity of potassium chloride solutions in dioxane-water mixtures, up to 50 per cent dioxane, at 35°C. were presented by Acharya, Das & Patnaik (81). They found the Jones-Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc^2$$

satisfactory for correlating their results. Viscosity, density, and also conductivity values for acetic acid in quinoline have appeared in the Russian literature (82), as have data on acetic acid in aniline (83), a review of work on ionic hydration in dilute aqueous solutions (84), and studies on ion solvent interaction by means of viscosity measurements (85).

This reviewer is of the opinion that a really sound theoretical approach to the general problem of ionic solvation must await a considerably better understanding of solvent structure than is yet available. This cannot serve, however, as a valid excuse for ignoring attempts currently made in this direction, and certainly not with regard to honest experimental work.

The possibility of calculating ionic hydration in salt solutions has been recently discussed by Darmois (86). Feates & Ives (87) discuss the ionization of cyano-acetic acid in relation to the structure of water and the hydration of ions and molecules, and van Ruyven (88) has attempted to determine the hydration of ions in concentrated solutions of electrolytes. He has also

considered the hydration of hydrogen, silver, and several bivalent ions (89, 90). The solvation of cupric ion in water-ethanol mixtures was reported on by Mine & Libres (91).

RUSSIAN CONTRIBUTIONS

Several Russian papers have already been mentioned (66, 67, 82, 83, 84) above. It has seemed convenient, however, to list together most of the relevant recent Russian literature, including some papers which would not normally fall within the scope of this review, limited as it is, but which, nevertheless, are of interest in the field of electrolytes.

Izmaïlov (92) has studied the solubility of silver dinitrophenolates in water and in methanol, and also these salts and the chloride, acetate, chloroacetate, benzoate, and salicylate optically in acetone and by emf. in dioxanewater (dielectric constant = 19.1). From these data and measurements on hydrochloric acid he computed dissociation constants and activity coefficients, and has discussed the possible role of solvation and of the dipole moment of the solvent species. In another paper (93) he proposed a logarithmic equation for conductivity analogous to the Arrhenius (activation energy) equation for viscosity, for aqueous solutions of strong electrolytes. In a study of the thermodynamic properties of alkali halides in formamide, methanol, ethanol, and butanol (94) he attempted to relate apparent activity to effects of solvation.

Galinker (95) reported a maximum in the specific conductance of aluminum chloride at 23 per cent in nitromethane from 20° to 40°C., which he attributed to a sharp increase of viscosity with increasing salt concentration. The temperature coefficient of conductance was negative below the maximum and positive beyond. He concluded that a complex was formed by the salt and solvent, that the viscosity was the dominant factor in the conducttance, and found the specific conductance-viscosity product to be linear with concentration.

Klochko (96) has discussed the temperature coefficients of conductance of pure and dissolved substances and reported (97) data on the conductance and viscosity of ammonium nitrate solutions in acetamide. The conductances of sulfuric acid, hydrochloric acid and nitric acid in aqueous solutions with their salts were measured by Muzyka (98). Complex ions of zinc, cadmium, and mercury in aqueous halide solutions (99), and of cobalt in citrate solutions (100) were reported.

Mishchenko & co-workers have determined the integral heats of solution and heat capacity for aqueous solutions of ammonium chloride (101) from 25° to 75°C. and from .01 M to saturation. They found

$$dC_p/dt = 0.00017 \text{ cal./gm. degree}^2$$

In another paper (102), in which the probability of formation of positive halogen ions in water is considered, they conclude that only I^+ might occur.

Obel'chenko (103) computed values for the constant, a, in the Debye-

Hückel second approximation for slightly soluble salts, using silver acetate, sulfate, and phosphate data (104).

Rutskov (105) has proposed that the volume of the solvent be assumed to vary rather than that of the solute in discussing apparent partial molar volumes in aqueous solutions of electrolytes. From deviations from additivity of the observed refracted indices of solutions with two solutes in water and in methanol, numerous ionic complexes have been postulated (106). In an interesting study of the velocity of sound in aqueous solutions of inorganic acids over a wide range of temperature and concentration, Mikhaĭlov and Shutilov (107) have found the compressibility $\beta = \beta_0 + Ac + Bc^{3/2}$, in which β_0 refers to the pure solvent. The acid solutions appear to be more complex than those of salts.

Regel (108) has described an interesting electrodeless method for measuring electrical conductance, based on inductance measurements by a rotating field. An electrodeless cell has also been described elsewhere (109).

Difficulties in calculating thermodynamic potentials in multicomponent solutions are the subject of a recent paper by Semenchenko (110). Mikulin (111) has considered a modification of the Debye-Hückel theory in which a decrease in the dielectric constant of the solvent in the vicinity of the ions is postulated.

The work of Frumkin on the potential difference at liquid-gas interfaces and on electrocapillary phenomena has been in progress for many years. The most recent papers have to do with studies on the cell (112)

$$+ N \text{ KCl} \left| \text{ solution} \right| \text{ air} \left| \text{ water} \right| N \text{ KCl}$$
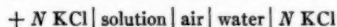
(in which, as in former work, polonium serves to ionize the air) and with the thermodynamics of electrocapillary phenomena in concentrated solutions (113). In the former paper values of 20, 14, 19 and 22 mv. were reported for 10^{-4} N HCl, $BaCl_2$, $La(NO_3)_3$, and $Th(NO_3)_4$, respectively. From measurements on the cell

$$.01 \ N \text{ KCl } (t_1°) \left| .01 \ N \text{ KCl } (t_2°) \right| \text{ air} \left| .01 \ N \text{ KCl } (t_1°) \right.$$
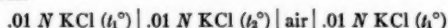
it was concluded that the temperature coefficient of the potential, solvent-air, is probably positive for ethanol and isoamyl alcohol, but negative for water and chloroform. Also, the water-air potential is estimated at 0.1 to 0.2 volt with the air negative. In the electrocapillary paper, the potential, ϕ, of mercury in a solution of a salt, KA, whose activity is a is taken to be

$$\phi_0 = \phi + \frac{RT}{F} \ln a$$

with respect to the reversible cation electrode in the same solution, and

$$(d\sigma/d \ln a)_{\phi_0} = RT \ (\Gamma_K + \Gamma_A)$$

in which σ is the interfacial tension and Γ refers to quantities adsorbed. On this basis, the relation of $d\psi/d\ln a$ to Γ_K and Γ_A was discussed, ψ being the adsorption potential.

A considerable number of papers dealing with fused salt systems have

appeared, but only a few seem relevant since most of them are of technical rather than theoretical interest. Koloti͡f, who had studied the behavior of a glass-tin-sodium electrode in several fused salts several years ago (114), has recently made a potentiometric study in fused silver and sodium halides (115). The temperature coefficients of ionic conductance of fused salts has been studied by Klochko (116). Samsonov reported studies on electrical conductance of transition metal compounds with boron, carbon, and nitrogen (117).

Here, mention must be made of Laity's study of transference and activity coefficients in fused salts (118, 119), and the very recent work of Sundheim on conductance and transference in molten salt mixtures (120).

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SOLUTIONS OF NONELECTROLYTES[1]

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Recent work on mixtures has shown a welcome concentration on funda-mental principles. An increasing number of papers has been published on both the theoretical and the experimental study of mixtures of simple and almost spherical molecules. It is from such studies that we must eventually obtain our knowledge of the relations, which are at present still imperfectly known, between the intermolecular forces in a liquid mixture and the excess thermodynamic properties of the mixture. The direct study of the two body forces themselves is best undertaken from the equilibrium and transport properties of gas mixtures at low pressures, and here too an increase in the amount of experimental work is very welcome.

Papers which contributed to this field were read at three of the confer-ences sponsored by the International Union of Pure and Applied Chemistry in July, 1957. The first was held in London and was entitled "The Thermo-dynamic and Transport Properties of Fluids" (1). The second was the 16th International Congress and was held in Paris. The section on diffusion in liquid mixtures was the most relevant to the subject of this review (2). The third was on the subject of the hydrogen bond and was held in Ljubljana, Yugoslavia (3). Papers from these conferences are cited below in the appro-priate sections. The proceedings of a symposium on statistical mechanics have recently been published (4). Some of these papers are also relevant to this section.

GAS MIXTURES

The second virial coefficient of a binary gas mixture is a quadratic func-tion of the mole fractions of the components, y_1 and y_2,

$$B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \qquad 1.$$

The middle coefficient, B_{12}, is determined solely by forces acting between a molecule of species one and a molecule of species two. Published values of such coefficients are still few, and those that extend over a wide range of temperature are very few indeed. Kramer & Miller (5) have measured this coefficient for helium + nitrogen at 30°C., and Harper & Miller (6) have measured it for helium+carbon dioxide. Their results agree well with the more extensive results of Cottrell, Hamilton & Taubinger (7, 8). Preliminary measurements have been made of the compression of hydrogen+nitrogen mixtures by Lialine *et al.* (9), and there are new measurements of the com-pression factor of argon+nitrogen by Ishkin & Rogovoya (10).

There is a direct method of measuring the coefficient B_{12} which avoids the disadvantage that the second term in equation 1 is always smaller than the

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sum of the other two terms. This method is the measurement of the concentration of a slightly volatile solid in a compressed gas. The gas acts as a solvent for the solid component. The leading term in a virial expansion for the increase in the concentration of the solid (component 2) gives directly B_{12}.

$$\ln \left(\frac{c_2}{c_2{}^0}\right) = \frac{V_{2}{}^{\bullet} - 2B_{12}}{V} + \frac{V_{2}{}^{\bullet}B_{11} - 3/2C_{112}}{V^2} + \cdots \qquad 2.$$

where $c_2{}^0$ is the concentration of the pure vapour in equilibrium with the solid, where V is the molar volume of the gas and $V_{2}{}^{\bullet}$ is the molar volume of the solid [Ewald et al. (11), Reuss & Beenakker (12)]. This equation is exact but converges slowly. Franck (13) has proposed a modification in which the second and higher terms on the right hand side are replaced by approximate expressions of the form of equilibrium constants. This modification improves the agreement with experiment at high densities.

An enhancement of the vapour pressure of liquid mercury by compressed gases was recently predicted on the basis of this equation by Jepson & Rowlinson (14) and has now been confirmed experimentally by Jepson et al. (15) who have derived values of B_{12} for mercury+propane and mercury+n-butane from 184 to 256°C. Such an enhancement must affect adversely the accuracy of gas isotherms measured in an apparatus in which the gas is confined over hot mercury. Saurel et al. (16) have designed an apparatus in which this difficulty is overcome by maintaining the gas-mercury interface in a cooled capillary.

Measurements of B_{12} are compared with values calculated from the properties of the pure components by using the following empirical equations for estimating the energy and collision diameter of the unlike interaction for a Lennard-Jones potential,

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{1/2}, \qquad \sigma_{12} = \tfrac{1}{2}\sigma_{11} + \tfrac{1}{2}\sigma_{22} \qquad 3.$$

The departures from these equations are usually satisfactorily small for simple molecules, but measurements over much wider ranges of temperature are needed before an adequate test can be made. The combination of the two methods discussed above would appear to be a suitable way to achieve this, as one method is applicable only at high and one at low temperatures.

The transport property that is most closely related to the unlike interactions in a gas mixture is the coefficient of interdiffusion, D_{12}. Schäfer & Moesta (17), and Schäfer & Schuhmann (18) have measured this coefficient for mixtures of argon with helium, neon, krypton, and nitrogen, and for mixtures of hydrogen and nitrogen. Their results cover wide ranges of temperature, the widest being that for argon+nitrogen which extends from 90 to 473°K. Unfortunately the results at low temperatures are less accurate than those at room temperature and the product $(D_{12}p)$ is not independent of pressure, p, owing to the imperfection of the gases. Nevertheless these very extensive results would probably repay analysis in terms of a more realistic

intermolecular potential than the square-well model employed by the authors.

Chou & Martin (19) have measured the rate of diffusion of carbon dioxide through hydrogen and through propane and have, rather surprisingly, found the product $(D_{12}\rho)$ to be almost independent of density, ρ, up to 250 atm.

The coefficient of thermal diffusion of a binary mixture is determined by the (1-1) and (2-2) forces as well as by the (1-2) forces, and so is not as direct a measure of the latter as is the coefficient of concentration diffusion. It is, however, a more sensitive test of the validity of an intermolecular potential. It was used, together with other coefficients, by Mason & Rice (20, 21) to establish combining rules for the (exp: 6) potential, similar to those of equation 3. B. N. Srivastava & K. P. Srivastava (22, 23) have re-examined the thermal diffusion coefficients of mixtures of argon with helium, neon, krypton and xenon, and mixtures of neon with krypton, xenon and nitrogen, and have proposed slightly different rules. B. N. Srivastava & Saxena (24) claim that the thermal conductivities of the three binary mixtures formed from neon, argon and xenon also fit better their revised combining rules. Raw & Kyle (25) have found the (12:6) potential and equation 3 to be adequate to fit the thermal diffusion coefficients of mixtures of hydrogen and boron trifluoride from 120 to 350°C.

Saxena (26), Mason (27), and B. N. Srivastava & K. P. Srivastava (22) have all considered the effects of the higher approximations in the kinetic theory of gases on the theoretical calculation of transport coefficients. Such corrections are most important in the calculation of the coefficient of thermal diffusion.

There is as yet no adequate theory of the transport properties at high gas densities, but Longuet-Higgins *et al.* (28) have extended their hard-sphere model to binary mixtures.

Van Itterbeek (29) has described the combined measurement of concentration and thermal diffusion.

Danby *et al.* (30) have shown that isomeric paraffin hydrocarbons can be separated by thermal diffusion—the less branched isomer going to the cold zone. Clarke & Ubbelohde (31) have found that straight paraffins have anomalous coefficients of diffusion through hydrogen and, to a lesser extent, through deuterium. Both experiments show that spherical potentials are inadequate for complex and flexible molecules.

The viscosity of a gas mixture is not so sensitive a test of the form of the potential or of the combining rules as either of the coefficients of diffusion, but it can serve as a useful check and is more easily measured. Rietvald & van Itterbeek (32) have found the (12:6) potential and equation 3 to be adequate for the viscosity of mixtures of neon and argon from 72 to 290°K. Kenney *et al.* (33) have measured the viscosity of mixtures of nitrogen and carbon dioxide up to 900°C. Their results are also adequately described by a (12:6) potential. Mueller & Lewis (34) have measured the viscosities of the

mixed vapours of iso-octane and perfluoro-n-heptane. The results do not show a linear dependence on composition but the deviations are smaller than might have been expected from the known abnormalities of the liquid mixture.

The conclusions that can be drawn from recent work on gas mixtures are (a) that a spherical (12:6) potential and equation 3 are adequate for most mixtures of the inert gases or of the inert gases with simple diatomic molecules, (b) that the use of an (exp: 6) potential and suitable combining rules is an improvement on a (12:6) potential at high reduced temperatures but not at low temperatures, and (c) that neither potential is adequate for polyatomic molecules.

Isotopic Liquid Mixtures

Mixtures of isotopes are ideal mixtures at temperatures high enough for the distinction between the quantal and classical descriptions of the systems to be negligible. Mixtures of helium isotopes at 1–2°K. and mixtures of hydrogen isotopes near 20°K. show positive deviations from Raoult's law.

Wansink & Taconis (35) have extended the earlier work of Taconis *et al.* (36) on the osmotic pressure of mixtures of He^3 and He^4 below the lambda-point of the latter. This unusual kind of osmosis is observed by using an annular slit of width 0.2 micron to separate the mixture from pure He^4. Such a narrow gap is permeable only to He^4, by virtue of its superfluidity, and so at equilibrium there must be a difference of pressure across the slit. Wansink (37) has calculated the excess free energy from these results and from the vapour pressure measurements of Sommers (38) and of Wansink *et al.* (39). His calculations indicate that phase separation should occur with an upper critical solution temperature of 0.7°K. Walters & Fairbank (40) have recently shown directly that such separation does occur and have found the critical temperature to be 0.8°K. Peshkov & Zinovieva (41) have succeeded in taking a photograph of the two phase system at 0.5°K. These results confirm the theoretical calculations of Prigogine *et al.* (42) who predicted a critical solution temperature below 1°K. and support their contention that the cause of the deviations from ideality is primarily the difference in the masses of the isotopes and not the difference in the kind of quantum statistics which they obey. Further measurements of the vapour pressure of mixtures rich in He^3 have been made by Peshkov & Kachinskii (43), and a review of the properties of both isotopes has been written by Hammel (44).

The deviations from Raoult's law of mixtures of hydrogen isotopes and of mixtures of ortho- and para-hydrogen are less striking, as the mixtures must be studied at higher temperatures. Friedman (45) has calculated, from published work, the excess properties of the latter mixture, which must be due to the differences in rotational energy and symmetry at low temperatures. Rietvald & van Itterbeek (46) have measured the viscosities of gaseous mixtures of H_2 and HD. The ratio of the viscosities of the pure com-

ponents departs from the square root of the ratio of the masses below 70°K. This result is probably due also to differences in rotational energy.

Nonpolar Liquid Mixtures

Mixtures of such simple liquids as the inert gases, methane, nitrogen, oxygen, and carbon monoxide are clearly the best systems with which to test the performance of statistical theories of solutions. In the past the available information has been confined to total and partial pressures, or to boiling points at fixed pressures. However, more serious attention is now being paid to these systems. The most useful results so far obtained are those of Staveley and his colleagues (47, 48) for the system methane+carbon monoxide at the triple point temperature of methane. They find the excess free energy to be symmetrical in the compositions with a maximum of 27 cal. mole^{-1}, the excess heat (measured directly) to have also a maximum of 27 cal. mole^{-1} but at a mole fraction of methane of 0.6, and the excess volume to be negative with a minimum of -0.33 cm.^{3} mole^{-1} at a mole fraction of methane of 0.4. The difference between the excess heat and the excess free-energy gives an excess entropy which is always small but which is positive in mixtures rich in methane and negative in mixtures rich in carbon monoxide. The theoretical interpretation of these results is discussed below.

Jeener (49) has reported some preliminary results for the system argon +methane at the same temperature. He has, like Staveley, measured directly the heat of mixing. He finds both excess heat and volume to be positive, the equimolar values being 20 cal. mole^{-1} and 0.2 cm.^{3} mole^{-1} respectively.

Cockett (50) is studying afresh the system nitrogen+oxygen, but the only results so far published are the partial pressures and boiling points at 1.32 atm.

Two ternary systems of slightly less simple molecules have been studied more extensively. Rowlinson *et al.* (51) have completed their measurements of the liquid-vapour equilibrium curves and the plait points of the three binary systems and of the ternary system formed from carbon dioxide, nitrous oxide, and ethylene. They showed that the properties of the ternary system are determinable from those of the binary systems by using the theory of conformal solutions. Haselden *et al.* (52) have continued their work on the related ternary system, carbon dioxide, ethylene, and propylene. Earlier work (53, 54) had covered the temperature, pressure, composition, and latent heats along the liquid-vapour boundaries. In the most recent paper there are volume measurements on the three binary systems for both orthobaric and unsaturated states and the calculation of some of the derived thermodynamic functions, including the excess heats and volumes in the supercritical region. When this programme is finished, it will provide ample material for the most rigorous testing of theories of solutions.

Mathieson & Thynne (55) have now completed the measurement of the

heats of mixing at 20°C. of all 10 binary mixtures formed from n-hexane, n-heptane, cyclohexane, benzene, and toluene. It has long been known that the excess heat of benzene+cyclohexane (195 cal. mole^{-1} in the equimolar mixture) is unusually large, and it has been suspected that the principal cause was the difference in molar volumes. It is therefore interesting to see that the excess heat of toluene+cyclohexane is also large (145 cal. mole^{-1} in the equimolar mixture). These components have almost identical molar volumes. In both cases the excess volume is positive with a maximum of about 0.6 cm.^{3} mole^{-1}. Rastogi & Varma (56) have measured the excess volume of benzene with toluene and with the xylenes. It is almost undetectable in the first system.

Moelwyn-Hughes & Missen (57) have measured the excess functions of the weakly polar systems formed from methyl iodide with methylene dichloride, chloroform, and carbon tetrachloride. The behaviour of the first and third system is quite unremarkable, but the second has a negative excess heat, free energy, and entropy, and an excess volume which changes from positive to negative with increasing concentration of chloroform. These results suggest some specific interaction between this pair of molecules.

Jeener & Lambert (58) have found that the negative excess volume of neopentane+carbon tetrachloride diminishes rapidly with increasing pressure and suggest that it may become positive at about 1000 atm.

A paper by Lu & Graydon (59) on an empirical calculation of volatility ratios provides a useful bibliography of measurements of liquid-vapour equilibria for mixtures of aliphatic and aromatic hydrocarbons. Smith (60) has reviewed recent measurements of vapour pressure, heats of mixing, equations of state, etc. Harper & Moore (61) have described another version of the equilibrium still, and Kapiustinski *et al.* (62) have described a precision gold microcalorimeter, sensitive to 5×10^{-5}°C., for the measurement of heats of solutions and of the heat capacities of solutions, primarily of electrolytes.

Reeves & Hildebrand (63) have measured the solubility of argon in organic liquids and Cook *et al.* (64), the solubility of hydrogen and deuterium. These papers form part of a concerted programme for which the apparatus has been described by Cook & Hanson (65). Clever *et al.* (66, 67) have measured the solubility of the inert gases in paraffin and aromatic hydrocarbons from 15 to 40°C. Loprest (68) has described another apparatus. In spite of the apparent simplicity of such systems their interpretation is probably quite as difficult as that of more conventional liquid-liquid mixtures.

FLUOROCARBON SOLUTIONS

There has never been any reason to suspect that a mixture of two fluorocarbons would show large deviations from ideality. This expectation has now been confirmed experimentally by Newcombe & Cady (69) and by Rowlinson & Thacker (70).

A few mixtures of fluorocarbons and inert gases have been studied recently. Thorp & Scott (71) found that carbon tetrafluoride+krypton was far from ideal with an excess free energy of 75 cal. mole^{-1} at 117°K. It is therefore surprising that Newcombe & Cady (69) found the solubility of gaseous argon in perfluoro-n-pentane to be ideal and that the figures of Reeves & Hildebrand (63) indicate a solubility greater than ideal in perfluoromethyl-cyclohexane. However, the concept of ideal solubility is not a precise one when it is applied to a gas above its critical temperature, and the evidence of Thorp & Scott must be accepted to show that such mixtures are probably far from ideal in the liquid state.

The greatest anomaly in this field is, however, the gross positive deviations from Raoult's law and the partial immiscibility of fluorocarbon+hydrocarbon mixtures. Scott (72) has made a critical review of this field and has summarised the experimental results on 63 systems. His conclusion is that there is no certain explanation of the anomaly but that the two most important effects are probably, (a) a difference in the radial form of the intermolecular potentials, and (b) a low value of ϵ_{12} due to the high ionisation potentials of the fluorocarbons. There seems little doubt that the anomaly is not due primarily to differences in molar volume. Jolley & Hildebrand (73) have shown that the same anomalous behaviour is shown towards octamethyl-cyclo-tetrasiloxane, a liquid whose large molar volume and low energy of vaporisation might have suggested that it should form an ideal mixture with a fluorocarbon.

Mueller & Lewis (34) have completed their study of the system iso-octane+perfluoro-n-heptane and have made the first calorimetric measurement of the heat of mixing in this field. The system follows the same pattern as those reviewed by Scott. Vreeland & Dunlap (74) have observed the effect of perfluoro-tri-n-butylamine on the system iso-octane+nitroethane which is already incompletely miscible. They find that a three phase system is formed at temperatures up to 34.8°C., which is 5.0°C. above the lowest of the three binary critical solution temperatures, that of iso-octane+nitroethane.

Rogers and his colleagues have measured the vapour pressures, densities, and electrical conductivities of mixtures of hydrogen fluoride with chlorine trifluoride (75), with bromine pentafluoride (76), and with iodine pentafluoride (77). In each case there is a large positive excess free energy and, what is more remarkable, a negative excess volume.

Banks & Musgrave (78) have found that mixtures of benzene and fluorobenzene are almost ideal.

POLAR AND HYDROGEN BONDED MIXTURES

There has been a considerable body of new experimental work in this field and there is space here only to list the more conventional papers. Excess volume of alcoholic solutions [Schultze (79)]; mixtures of ethanol and

isopropanol with hydrocarbons [Brown *et al.* (80)]; mixtures of methanol with chloromethanes [Moelwyn-Hughes & Missen (81)]; mixtures of acetone and chloroform [Röck & Schröder (82)]; mixtures containing butyl acetate [Röck & Rothe (83)], and benzyl acetate [Moore & Styan (84)]; aqueous solutions of dioxan [Malcolm & Rowlinson (85)], of pyridine and substituted pyridines [Andon *et al.* (86)], of glucose [Young (87)] and of higher sugars derived from cellulose [Taylor (88)].

Aqueous solutions may be characterised by the chemical nature of the solutes which may be correlated with the excess functions and with the phase behaviour of the solutions [Rowlinson (89)].

Crützen *et al.* (90) have made a very detailed study of the liquid-vapour equilibria, excess heats, excess heat capacities, and liquid-liquid miscibilities of all six binary mixtures and of three of the ternary mixtures formed from glycol, aniline, N-methyl aniline, and NN-dimethyl aniline. A wide range of behaviour was found from ideality to azeotropy and partial immiscibility. The results are presented in 64 tables.

Kohler & Rice (91) have made another detailed study of the shape of the coexistence curves at the lower critical solution temperature of water+triethylamine. Copp & Everett (92) have discussed the relations between the algebraic form of the excess free energy and the shape of the coexistence curve. Cox & Herington (93) have shown that near 12 upper critical solution points and near 4 lower critical solution points, the compositions of the coexisting phases (prime and double prime) are well represented by

$$\ln\left[\frac{x_1' \, x_2^c}{x_2' \, x_1^c}\right] = \ln\left[\frac{x_2'' \, x_1^c}{x_1'' \, x_2^c}\right] = A \mid T - T_c \mid^{1/3} \qquad 4.$$

where A is an empirical parameter which is approximately the same for both branches of the coexistence curve. The equation is remarkably successful and without theoretical basis. Claesson & Sunderlof (94) have measured coefficients of diffusion near critical points.

Schneider and his colleagues (95, 96, 97) have used the method of nuclear magnetic resonance to detect hydrogen bonding between hydrogen chloride and chloroform on the one hand, and the π-electrons of olefines, acetylenes, and benzene on the other. Such nonlocalised bonds would appear to be of a type intermediate between conventional hydrogen bonds and the electron transfer complexes reviewed in the next section. The perturbation of conventional hydrogen bonds by solvent molecules is still a frequent subject for study by the methods of infrared spectroscopy (98 to 101). Perhaps the most interesting of recent papers are those of Becker (102, 103) who has made a careful study of the infrared spectrum of methanol in carbon tetrachloride and has reported a surprisingly high heat of dimerisation of 9000 cal. mole^{-1}. The heat of polymerisation to larger groups is only about half this size.

INTERMOLECULAR COMPLEXES

Electron transfer complexes have been studied recently by spectroscopic rather than by thermodynamic methods. An exception is the demonstration

by Shinoda & Hildebrand (104), by means of measurements of solubility and of partial molar volume, that iodine forms a complex with tetraethoxy-silane, $(C_2H_5O)_4Si$, but not with octamethyl-cyclotetra-siloxane, $(CH_3)_8Si_4O_4$. In the former molecule the oxygen atoms are exposed, but in the latter they are hidden in an inner shell behind a barrier of methyl groups and the iodine molecules are unable to approach them.

There is in this review space only for a list of other systems that have been studied in the past year, mainly by spectroscopic methods. In each case the Lewis acid, or electron acceptor, is listed. The base, or donor, is usually an aromatic substance.

Bromine [Slough & Ubbelohde (105)], iodine [De Maine (106, 107)], Ferguson (108)], sulphur dioxide [De Maine (109)], nitrogen tetroxide [Addison & Sheldon (110)], hydrogen chloride [Strohmeier & Echte (111)], and chloranil [Peticolas (112)].

De Maine *et al.* (113) have studied the dimerisation of nitromethane in carbon tetrachloride and in cyclohexane.

THEORY

In the last two years there has been an almost complete abandonment of the lattice model of liquid mixtures, and instead, a development of methods based upon the principle of corresponding states. Much of this work was reviewed in detail last year by Z. W. Salsburg, but new work makes it necessary to return to the subject again this year. An account of both the lattice theories and some of the newer nonlattice theories has been given in a recent book by Prigogine (114). (The book deals also with the contributions of the Brussels school to the theory of isotopic mixtures, polymers, and polar solutions.)

A central feature of theories of solution based upon the principle of corresponding states is the importance given to the concept of a random mixture. This concept is the starting point of the recent work of Prigogine *et al.* (115), of Scott (116), and of Brown (117), the last of whom formulates it as follows:

The potential energy of a pure substance in any arbitrary configuration, Q, may be denoted $\Phi(Q)$. In a mixture Φ will depend not only on the configuration of the molecules but also on the assignment τ of the various species to the positions in space specified by the configuration Q. The approximation of a random mixture is that of replacing $\Phi(Q, \tau)$ in the partition function by its *a priori* average over all assignments denoted $\langle \Phi(Q) \rangle$.

The Helmholtz free energy is therefore given by,

$$A = -kT \ln \left[\frac{1}{\Pi_i N_i!} \int \cdots \int \exp \left[-\langle \Phi(Q) \rangle / kT \right] dQ \right] \qquad 5.$$

The configurations, Q, are not restricted to those of a regular lattice but include all possible positions in a given volume. This free energy may be related exactly to the experimental thermodynamic properties of any of the

pure components by equations involving the intermolecular force constants, if, and only if, the potentials are all of the Lennard-Jones $(n:m)$ form, with the same values of n and m. Brown (117) and Chaundy & McLeod (118) have shown rigorously that this condition is necessary and that the more general relation

$$\epsilon_{ij} = l_{ij}\epsilon_{00}\cdot f(m_{ij}\sigma_{00}/r) \qquad \qquad 6.$$

(where l_{ij} and m_{ij} are characteristic parameters of the i-j interaction) is not adequate. The most important application of this approximation has been to binary mixtures whose potentials follow equation 3. The predicted excess Gibbs free energy and excess enthalpy are always positive, but the excess entropy and volume may have either sign. Both are negative if the sizes of the molecules are equal. These predictions are generally in agreement with experimental results on simple systems. For example, the system methane +carbon monoxide, which was discussed above, has a positive excess free-energy and enthalpy and a negative excess volume. However, the excess entropy changes sign with changing composition—a result which is not in accord with the theory. The successes and failures of this treatment make it clear that equation 3 is of very limited application. It is not, for example, entirely adequate for the system methane+carbon monoxide; it is inadequate for solutions of aromatic molecules (55, 56); it is inadequate for fluorocarbon solutions (72); and is clearly unsuitable for polar and nonspherical molecules even if the polarity is that of a simple quadrupole, as in carbon dioxide and acetylene (51, 119).

Improvements to the random mixing approximation can be made in two ways. First, the restriction to spherical molecules can be removed. Balescu (120) has made a start here by considering the effects of weak dipoles. Secondly, the ordering effects in mixtures of spherical molecules can be examined. This has been done by Brown (121) and by Kirkwood and his colleagues (122, 123), by using the moment expansion. If δA is the difference in free energy between the real system and some known system (pure substance, ideal mixture or random mixture) then

$$e^{-\delta A/kT} = e^{-\overline{\delta\Phi/kT}} \qquad \qquad 7.$$

where the bar denotes a Boltzmann average over all configurations, Q. This can be written as an expansion of moments,

$$e^{-\delta A/kT} = 1 - \frac{\overline{\delta\Phi}}{kT} + \frac{\overline{(\delta\Phi)^2}}{2(kT)^2} + \cdots \qquad \qquad 8.$$

or as an expansion of cumulants,

$$\delta A = \overline{\delta\Phi} - \frac{\overline{(\delta\Phi - \overline{\delta\Phi})^2}}{2kT} + \cdots \qquad \qquad 9.$$

The first term in this equation, $\overline{\delta\Phi}$, vanishes if the known system is chosen to be a random assembly. The second order term may be related to statistical,

but nonthermodynamic, functions of a pure component only for mixtures of Lennard-Jones molecules. These nonthermodynamic functions are called fluctuation integrals by Brown. He shows that they can be related to thermodynamic functions for a cell-model of the liquid, but only at the cost of some inconsistency implicit in the nature of this model. His calculations show that this ordering reduces the large positive excess free energy predicted by the random mixture approximation for mixtures of molecules of different sizes.

Closely related to this method is the local or semi-random mixing approximation which is applicable only to a cell-model (114, 115). In this it is assumed that the neighbours of any one molecule are randomly chosen from the species present in the mixture. This approximation also predicts a lower excess free energy than that for the random mixture, particularly for molecules of different sizes, but only at the cost of introducing the cell-model and of making an assumption about the sizes of the cells. This assumption is that the sizes are chosen to minimise the free energy. It is reasonable but essentially arbitrary.

The restriction to Lennard-Jones molecules may be avoided by making the expansions of equations 8 and 9 about the ideal mixture and not about the random mixture. However, the convergence is now naturally less rapid as the first order term no longer vanishes but is the first order term of the theory of conformal solutions of Longuet-Higgins (124). Brown (125) has shown that the second order terms cannot be expressed in terms of the thermodynamic functions of a pure component, and it appears that this expansion will probably be less useful than that about the random mixture. It may serve, however, as a useful critique for future developments.

Barker (126) has proposed a different expansion, which he calls a cluster expansion from its resemblance to the cluster expansion of the theory of imperfect gases. He puts

$$\delta\Phi = \sum_{i>j}\sum (\delta\phi_{ij}) \qquad\qquad 10.$$

$$\alpha_{ij} = \exp\left[\,\delta\phi_{ij}\right]/kT] - 1 \qquad\qquad 11.$$

where ϕ_{ij} is the energy of interaction of a pair of molecules, i and j. This gives

$$e^{-\delta A/kT} = 1 + \overline{\prod_{i>j}\prod (1 + \alpha_{ij})} + \cdots \qquad\qquad 12.$$

or

$$\delta A = -kT\overline{\sum_{i>j}\sum \alpha_{ij}} + \cdots \qquad\qquad 13.$$

Barker suggests that the random mixture is again the most suitable state about which to make this expansion.

Hill (127, 128) has proposed an unsymmetrical expansion of the type first suggested by McMillan & Mayer (129). The thermodynamic properties

of the mixture are to be expressed as power series in either the molality or mole fraction of the solute. No numerical results have yet been published.

Münster & Sagel (130) have discussed the determination of the degree of departure of a real mixture from a random mixture by the use of the x-ray diffraction patterns.

The critical temperatures of two fluids whose potentials may be related by equation 6 are in the ratio of their intermolecular energies, ϵ. This does not hold exactly for a mixture as the gas-liquid plait-point is determined by the breakdown of material (or diffusional) stability and not by the breakdown of mechanical stability. Nevertheless, if plait-point temperatures, pressures, and volumes could be exactly related to intermolecular parameters, then they would provide one of the most accurate methods of measuring ϵ_{12} and σ_{12}, and so of checking equation 3. A start has been made by Bellemans et $al.$ (131, 132) who have deduced these relations to the first order for a conformal mixture and to the second order for a random mixture. A minimum in the plait-point temperatures requires that ϵ_{12} is lower than both ϵ_{11} and ϵ_{22} only if the molecular sizes are equal.

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THE SOLID STATE[1]

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In selecting subjects for review, I have necessarily omitted some important areas of research, for which a few words of explanation are in order. I have referred hardly at all to the properties of semiconductors, which previous articles in this series have treated at some length; the existence of numerous other reviews of this subject, and indeed of at least one annual volume entirely devoted to it, seems to guarantee that no one will suffer from the lack of a brief survey here.

I have omitted all reference to ferroelectricity, since I could add nothing to the excellent review by Känzig (1). Optical properties of solids have been omitted with regret, but this deficiency is compensated by the appearance of the article on luminescence by Klick & Schulman (2), and the promise of others in this area in later volumes of *Solid State Physics*.

I am deeply indebted to many of my colleagues, who have so generously taken the trouble to discuss their special fields with me at all stages in the preparation of this review.

General Theory of Crystals

Theory of the electron gas.—The starting point for much theoretical work on the properties of crystals of the metallic and semiconductor type is the assumption that the valence and conduction electrons can be treated as free particles. This crude approximation is then usually refined by perturbation calculation of the influences on the electrons of (a) the electrostatic interactions of the electrons themselves, and (b) the ions at the lattice sites. An important advance with respect to the first of these is found in a remarkable series of papers by Gell-Mann, Brueckner, Sawada, Fukuda & Brout (3–7), whose results we summarize in some detail. The total electron energy ϵ (measured in rydbergs, $me^4/2\hbar^2$), can be expanded as a series in the perturbation parameter, r_s, the radius (in units of the Bohr radius, a_o) of a sphere whose volume is the average volume per electron. The perturbation series is valid for small r_s (high density). The first term in the series is the Fermi energy, $3r_s^{-2}/5\alpha^2$, $(\alpha^3 = 4/9\pi)$. The second term is the exchange energy, $-3r_s^{-1}/2\pi\alpha$, which is the electrostatic energy for free electrons. The rest of the energy, ordinarily called the "correlation energy," is represented by terms in higher powers of r_s, the leading ones being a constant term and one proportional to $\ln r_s$. If these terms are calculated in a straightforward way, the result is infinite, essentially because the long range Coulomb force causes an infinite amount of small angle electron-electron scattering. Gell-Mann & Brueckner (3) have used a technique derived from quantum electrodynamics to eliminate this divergence and obtain for the correlation energy

[1] The survey of literature pertaining to this review was concluded December, 1957.

$2\pi^{-2}(1-\ln 2) \ln r_s - 0.096 + O(r_s)$. This result, which is exact in the limit of high density, is finite because the Coulomb force is largely screened beyond a radius $r_s^{1/2}a_o$, as has been shown by Bohm & Pines (8). The Bohm-Pines (BP) expression for the correlation energy, as corrected by Gell-Mann & Brueckner, differs from the result above only in giving the value -0.158 for the constant term. Gell-Mann (4) has extended the calculations to obtain the lowest excited states of the electron gas, namely those which in the unperturbed state would be described as excitations of a single electron out of the Fermi sea. In this way he obtains the low temperature heat capacity of the electron gas with correlation, which differs from that of the gas without correlation by a factor $[1-0.083r_s(\ln r_s+0.203)]^{-1}$; the BP result is $[1-0.083r_s(\ln r_s-1.47)]^{-1}$. The preceding exact results have also been derived by Sawada (5) without the use of perturbation theory. The Sawada technique has been further developed by Sawada *et al.* (6) and Brout (7) to exhibit more clearly the connection with the BP theory. The eigenvalue problem which must be solved has, in addition to a continuous spectrum corresponding to one-electron excitations, a set of bound states corresponding to the plasma excitations ("plasmons") appearing in the BP theory. For sufficiently large energies, the plasmon spectrum merges with the continuous spectrum, and there arises thus a natural momentum cutoff beyond which the plasmon description is inappropriate.

Various controversial aspects of the BP theory are discussed by Sawada *et al.* on the basis of their more rigorous results, and it is concluded that the the former provides excellent physical insight, although it is only semi-quantitative.

The BP theory has stimulated much activity, particularly with regard to the interpretation of the energy losses of fast electrons passing through solid films. The experimental situation has been critically discussed by Marton (9), and the methods and results have been reviewed by Friedmann (10). The interpretation of the mechanism of the characteristic losses is still somewhat controversial [Sternglass (11); Leder, Mendlowitz & Marton (12)], but it seems likely that only a part of the observations can be explained as one-electron excitations. Pines (13) has attempted an extensive correlation of the BP theory with experiment, and more recently Raimes (14), reviewing the theory of plasma oscillations, has concluded that the energy loss experiments argue strongly for the reality of plasmons. That the simple BP theory often gives values for the energy losses in close agreement with experiment must be regarded as fortuitous, in view of its rather large deviations from the more exact theory of the same model (3 to 7).

Thanks to the existence of Raimes' review (14), it is necessary only to mention the most recent papers in this area. In a series of publications, Ferrell and Ferrell & Quinn (15, 16) have obtained new insights into the collective aspects of the motion of an electron gas. In his latest work Ferrell has arrived at a point of view very like that of Gell-Mann & Brueckner, Sawada *et al.*, and Brout (3 to 7), insofar as comparison is possible, since

Ferrell's emphasis has been on the interpretation of the energy loss experiments. Ritchie (17) has treated the plasma excitation problem on the basis that the electrons may be characterized by a frequency and wave vector dependent dielectric constant, and has obtained the BP dispersion relationship, among other results. Krisement (18), comparing the BP theory with the older Wigner-Seitz method, has shown that they have much in common, and that there is implicit in the older theory also a "cut-off" wave length of about the same size as in the newer. The much vexed question of the "subsidiary conditions" in the BP theory has been reconsidered by Bohm, Huang & Pines (19), who conclude that these conditions are compatible with the approximations made in obtaining the Hamiltonian and energy of the many electron system, and that their effect on the ground state energy and specific heat is small, [cf. Sawada *et al.* (6)]. Kanazawa (20), on the contrary, concludes that these conditions are so stringent that they cannot be satisfied by any wave function, although a modification which removes the inconsistency is possible. The extension of the collective description to electrons in a crystalline field has continued to progress. Pines and Nozieres (13, 21, 22) conclude that the BP theory is applicable with some modifications, provided there is not an important part of the one electron excitation spectrum at energies comparable with the plasmon energy. A quite different approach to the same problem has been presented by Ichikawa (23).

Quantum theory of electrons in crystals.—Löwdin (24) has reviewed the theory of the cohesive properties of solids, particularly the alkali metals and ionic crystals, from a unified point of view which emphasizes the utility of the density matrix and the "tight binding" approach. The orthogonalized plane-wave (OPW) method has been reviewed by Woodruff (25); Fukuchi (26) has used this method to calculate the band structure of copper, and Callaway & Haase (27) have applied this method to cesium. Heine (28) has shown that the convergence of the OPW method can be much improved by a proper choice of the atomic like wave functions, and has calculated the band structure of aluminum in great detail [see also *Galvanomagnetic and related effects*].

Callaway, Woods & Sirounian (29) have shown that relativistic effects have a negligible influence on the cohesive energy of the alkali metals, although this results from a near cancellation of much larger individual contributions. On the other hand, Callaway (30) has demonstrated by a perturbation calculation that core polarization may give a substantial contribution to the binding energy of the alkali metals, especially those of greater atomic number.

Mott & Stevens (31) have discussed the band structures of the transition metals in relation to a number of important physical properties.

The way in which a crystal changes from an insulator to a metallic conductor as the interatomic distance is decreased has been treated by Mott (32), who concludes, contrary to the usual view, that for both monovalent and divalent atoms the transition is discontinuous, being connected with a

sudden alteration in the form of the ground state wave function. Using the conventional criterion of band-overlap, ten Seldam (33) has calculated the density at which electronic conductivity would appear in solid helium; the values obtained, which are, of course, very high, are quite sensitive to the method of approximation.

An approach which has been successful in accounting for the structures of metal complexes has been extended to the crystal structures of transition metal oxides by Dunitz & Orgel (34). The distortions from cubic symmetry in these oxides (especially spinels) are related to the splitting of the metal ion d orbitals in the crystal field, which gives rise to a sort of Jahn-Teller effect. Similarly, Orgel (35) has shown that elements with an odd number of d electrons in a body-centered cubic structure may be expected to distort somewhat to structures of lower symmetry, as is observed.

Nonelectronic general theory.—A classic problem in calculating the cohesive energy of ionic crystals is the evaluation of the inter-ionic electrostatic energy, i.e., the calculation of Madelung constants. Although such calculations have been made during the past fifty years, it was not realized until quite recently that there exist simple linear relations between the Madelung constants of various structures. The first proof of such relations seems to have been made by Naor [unpublished; see Fumi & Tosi (36)]. Improved methods for computing Madelung constants by means of rapidly convergent series are given by Benson & van Zeggeren (37) and MacKenzie (38), and an application to the surface energies of the alkali halides has been made by van Zeggeren & Benson (39). A method for improving the convergence of some lattice sums of general types, including Madelung constants as a special case, has been devised by Nijboer & de Wette (40). Raynor, Naor & Tyzack (41) have shown how Madelung constants may be computed for structures which are formed by various stacking sequences of hexagonal close-packed layers.

Thermodynamic formulas for crystals in a general state of elastic strain have been derived by MacDonald (42) and by Ting & Li (43). Fullman (44) has shown that if the surface free energy of a single crystal is sufficiently anisotropic the equilibrium form may be a polycrystal.

EXPERIMENTAL DETERMINATION OF ELECTRONIC STRUCTURE

Galvanomagnetic and related effects.—Although in principle every property of a crystal gives some information about its electronic structure, certain properties stand out by virtue of the directness with which they can be related to the distribution of the electrons in space and momentum. As is well-known, the de Haas-van Alphen effect and similar oscillatory magnetic effects, cyclotron resonance, and optical absorption have been very useful in elucidating the band structures of silicon, germanium, and other semiconductors. Lax (45) has summarized the results of these experiments, the interpretation of which has been intimately connected with progress in the theory of the band structures of the substances investigated. For metals,

except for the borderline case of bismuth, the present state of information is far behind that for nonmetals. Chambers (46) has given an excellent survey of the experimental methods, their potentialities and limitations, and of the fragmentary results. Cyclotron resonance of a sort is still possible in metals even though the radiofrequency field penetrates only slightly, provided the constant magnetic field is nearly parallel to the surface [Azbel & Kaner (47)]. Heine (48) has examined theoretically the conditions for cyclotron resonance in metals, using the ineffectiveness concept of Pippard. His conclusions differ from those of Azbel' & Kaner essentially only in that he finds a much less stringent criterion for the parallelism of the magnetic field to the surface. Resonance has been observed in very pure tin at liquid helium temperatures by Kip *et al.* (49) even when the angle between the magnetic field and the surface was as much as 30°, so it seems that Heine's criterion is correct. Kip *et al.* also found numerous subharmonics, as predicted; no interpretation in terms of band structure is given in their preliminary report. Cyclotron resonance in bismuth, as detected by Aubrey & Chambers (50), gives a model of the Fermi surface in reasonable agreement with that from the de Haas-van Alphen effect. The classical and quantum theory of cyclotron resonance in metals has been further developed by Mattis & Dresselhaus (51).

The de Haas-van Alphen effect of aluminum has been measured by Gunnerson (52). His results, in conjunction with the data on the anomalous skin effect and low temperature heat capacity, have been used by Heine (28) to obtain a very complete picture of the Fermi surface. Heine made minimum use of theoretical calculations of the band structure, although those parts of the Fermi surface which are remote from any zone boundary had to be calculated, since they contribute only an unobserved very rapid period to the oscillations of the magnetic susceptibility as a function of field.

The theoretical treatment of galvanomagnetic effects is relatively easy only when the Fermi surface bounds simply connected regions of momentum space lying within a Brillouin zone, or, when the Fermi surface extends across zone faces, if the various parts can be rearranged to form a simply connected surface. In the more general case, the electron orbits may extend over more than one zone before closing, or even may not close at all. The complex phenomena associated with this situation are just beginning to be analyzed theoretically. Lifshitz, Azbel' & Kaganov (53) discuss this case as part of a general theory of electrical conductivity and Hall effect in metals in high magnetic fields. Brailsford (54) has treated a simple band model which has some unclosed orbits; he finds that the usual semi-classical quantization rules hold well for the closed orbits, but that level broadening occurs when the orbits are nearly open, and that the "open" orbits form a continuum in a nonvanishing magnetic field.

A proposal for a new resonance method has been made by Pippard (55). Noting that Bömmel (56) found a periodic dependence on magnetic field of the ultrasonic attenuation in tin at 4°K., Pippard suggests that the energy

transfer is from the sound field to electrons moving in orbits of diameters equal to an odd multiple of half the sound-wavelength. Measurement of the resonant field as a function of crystal orientation may, therefore, give just the same kind of information about the Fermi surface as is deduced from cyclotron resonance.

Jan (57) has recently reviewed the subject of galvanomagnetic and thermomagnetic effects in metals.

Positron annihilation.—Energetic positive electrons are apparently brought to thermal equilibrium in condensed matter very quickly, and subsequently annihilate with negative electrons. The decay products are two or three γ-rays, depending on whether the negatron spin is antiparallel or parallel to that of the positron. Free $e^+ - e^-$ pairs have a much shorter lifetime (1.25×10^{-10} sec.) for the two γ process than for the three γ process (1.4×10^{-7} sec.); in either case, the γ-rays have no net momentum in the center-of-mass system of the original pair, so that for the two γ process the photons are emitted with equal energy at precisely 180° to each other, if the original pair was at rest. In the center-of-mass system of a crystal the pair may have had some momentum before annihilation, and this appears as a (small) deviation from 180° of the angle between the paths of the photons. Thus measurements of the angular correlation of the photons give information about the momentum distribution of the annihilating pairs, which would be essentially that of the electrons, if the perturbation due to the positron were negligible. The experiments summarized by Berko & Hereford (58) indicate that in many crystals, including all metals studied, the decay scheme is much like that for free positronium, and that the angular distribution can be accounted for quite well by a Fermi distribution of the electron momenta. Stewart (59) has published the results of angular correlation measurements on 34 elements, mostly metals, and these, too, are adequately described as arising from a Fermi distribution of the valence electrons with an additional high momentum component coming from the core electrons. However, Berko, Kelley & Plaskett (60) have found that the annihilation radiation from oriented graphite crystals seems to be related to the momentum distribution of the valence electrons, and that the *1s* electrons do not annihilate. The results were not in agreement with those calculated assuming a free positron wave function and a molecular-orbital wave function for the valence electrons. Angular correlation studies on Mg and a number of alkali halides have been made by Millett & Castillo-Bahena (61). The momentum distribution which they found for NaCl could be accounted for by assuming that the positron is bound to the Cl⁻ in an *s* state, and that it annihilates with a closed shell electron. In reviewing the theory of these effects, Ferrell (62) states that the agreement observed is encouraging enough to warrant much more theoretical effort; he shows that the annihilation rate and momentum distribution in many cases depend on only the product of the positron and electron wave functions, the latter, however, being distorted by the presence of the positron.

In liquids and noncrystalline materials, the decay process is much more complex than in the free state or in crystals. A description of these results would be out of place here; we may, however, note that Landes, Berko & Zuchelli (63) have demonstrated a large difference in the positron lifetimes in solid and liquid naphthalene, the change occurring quite sharply at the melting point.

The fact that parity is not conserved in β-decay, and that positrons may, therefore, be spin-polarized with respect to their direction of motion, has already penetrated into solid-state physics. Hanna & Preston (64) observed that the rate of the two γ decay of positrons in iron was enhanced by magnetizing the iron in a direction parallel to the positron motion. In the magnetized state, the positrons encountered electrons with spins antiparallel to their direction of motion more often than in the unmagnetized state, and the increase in the two γ process (positron and electron spins opposed) implied that the positron spins were directed parallel to their direction of motion.

ELASTIC PROPERTIES OF CRYSTALS

Theory.—The form of the potential energy of a crystal as a function of the nuclear coordinates has been reconsidered by Laval (65) from an atomistic viewpoint. When interactions between three atoms are considered in addition to those between pairs only, as heretofore, results at variance with classical theory are obtained. For example, a total of 45 static and 36 dynamic elastic coefficients are required for triclinic crystals, rather than the usual 21. The theory is supported by some experiments of Le Corre (66).

Rosenstock (67) has derived relations between the numbers of critical points in the vibrational spectrum occurring within a three-dimensional region in reciprocal space and the numbers of such points on the surface of the region. Mathematical methods suitable for the spectra of cubic crystals have been given by de Launay (68) and Budzinski & Schiff (69). Genensky & Newell (70) have treated analytically the model of a chain polymer crystal discussed by Stockmayer & Hecht (71). Because of the use of an angle-bending force constant, the singularities are of a different nature than anticipated by Van Hove; nevertheless his methods were very useful in analyzing the complex spectrum.

The theories of the vibrations and of the electronic energy bands of crystals have much formal resemblance. Useful analogies remain even when perfect periodicity is no longer present, as is discussed in a review of semiconductor alloys by Herman *et al.* (72). A new method of treating the disordered linear chain [Des Cloizeaux (73)] gave the same results as were obtained earlier. There have also appeared calculations of the vibrations of a linear chain as affected by free ends [Wallis (74)] and by impurities [Bjork (75)]. Rosenstock (76) has asserted that the boundary conditions also play a role in determining the absorption spectrum of a crystal.

Experiment.—Values of elastic constants of anisotropic materials have

been collected by Hearmon (77). The results for diamond given by McSkimin & Bond (78) differ much from older values. Ultrasonic measurements of elastic constants have been made for LiF by Briscoe & Squire (79), for Mg by Long & Smith (80), and for Mg and some dilute alloys by Slutsky & Garland (81). The last results are in accord with an atomic model which includes a bulk contribution from the conduction electrons. The elastic constants of numerous substances have been determined from their diffuse x-ray scattering by Wooster and co-workers. References are given by Prasad & Wooster (82).

A very complete analysis of the vibrational spectrum of aluminum has been carried out by Walker (83), who measured the diffuse x-ray scattering and separated the thermal part from the Compton contribution by a self-consistent method. These results, in conjunction with values of the elastic constants, fixed nine atomic force constants, which were then used in a Born-von Karman calculation of the vibrational spectrum.

A more direct approach which is only beginning to be exploited is to measure the inelastic scattering of very slow neutrons. Conservation of energy and momentum are sufficient to determine dispersion curves (frequency vs. wave number) for elastic waves moving in various directions. Aluminum has been studied in this way by Carter *et al.* (84) and by Brockhouse & Stewart (85), with results generally in good agreement with those from x-ray scattering (83). Germanium has been studied by Brockhouse & Iyengar (86), and another method suitable for completely incoherent scatterers has been applied to vanadium and an alloy of cobalt and manganese by Stewart & Brockhouse (87).

The temperature dependence of the heat capacity of four alkali halides has been used by Berg and associates (88, 88a) to derive various details of the vibrational spectrum. The anharmonicity of crystals is treated in terms of Grüneisen parameters by Barron (89).

ELECTRONIC TRANSPORT PHENOMENA

The conventional theory of transport phenomena starts from the Boltzmann equation. The calculation of the electrical conductivity and similar properties reduces to the evaluation of certain integrals containing a momentum-dependent relaxation time, which must be calculated from the scattering mechanism(s). The integrals involve also an equilibrium momentum distribution function, usually that for free electrons. This theory, which has been reviewed very recently by Blatt (90), has been and will doubtless continue to be very useful. However, it is becoming increasingly apparent that a rigorous treatment of time-dependent processes can lead to a more satisfactory understanding of electrical conduction and other transport phenomena, particularly those in strong external fields [see Argyres (91)]. The incentive to develop such rigorous theories has come in part from the desire to formulate a fundamental statistical mechanics of irreversible processes in general, as well as from a recognition that the Boltzmann equation

is not valid in certain special situations in solids. Work in this area is being carried on simultaneously in many places, and concrete results are just beginning to appear. Therefore, it is possible only to stress the importance of this trend for the near future, and to cite a few contributions.

Brief surveys have appeared of the work of Prigogine (92) and of Kubo (93). A paper on the quantum theory of irreversible processes by Prigogine & Toda (94) contains references to previous work. An exposition of his general theory, with applications to magnetic and electrical conduction problems, has been given by Kubo (95). Kubo, Yokota & Nakajima (96) have extended the theory to situations involving thermal gradients as well as external electromagnetic fields. The Kubo method has been applied to electrical conduction by Nakano (97). Kohn & Luttinger (98) have calculated the density matrix for a system of electrons being scattered by random impurity centers, and have shown that an expansion in powers either of the scattering strength or of the density of scatterers gives the Boltzmann equation in lowest order.

Using the classical approach, Hanna & Sondheimer (99) have shown that thermal conductivity and thermoelectric power may be considerably affected by deviations from thermal equilibrium.

White and coworkers (100, 100a) have measured the thermal and electrical conductivities of a number of transition metals. The temperature dependence has been interpreted by them in terms of the various possible mechanisms of scattering. Overhauser & Schindler (101) have attributed the asymmetrical variation with concentration of the residual resistivity of Ni-Pd alloys to a spin dependence of the scattering process [see also Schmitt & Jacobs (102)]. Blatt (103) has discussed the difference between elements of the Ag group and those of the Cu group as solutes in Ag and Cu with regard to the residual resistivity produced; the Friedel sum rule, modified to include volume changes, is used to fix the scattering potential, and the calculated resistivities are then in very good agreement with experiment.

MAGNETISM (EXCEPT DIAMAGNETISM)

Although this subject is treated here at somewhat greater length than in earlier reviews in this series, it has not been possible to do more than to indicate some important lines of activity by describing the recent results in them.

General theory.—The exact statistical treatment of three-dimensional models of magnetism remains an unsolved problem, but various approximate results continue to be obtained. The so-called constant-coupling approximation developed by Kasteleijn & Kranendonk (104, 104a) is the equivalent in accuracy, for the Heisenberg model, of the quasi-chemical method for Ising systems, and may be expected to be as useful as the latter for the calculation of equilibrium properties. Temperley (105) has shown that boundary conditions have no effect on the behavior of a two-dimensional Ising lattice near its Curie temperature. Danielian & Stevens (106) have used the

first few terms in the high-temperature expansion of the exact formula for
the susceptibility of a face-centered cubic antiferromagnet to show that it
is necessary to go to very high temperatures indeed before graphs of $1/\chi$
against T are sufficiently linear to enable accurate estimation of the Curie
temperature and Curie constant. According to Kondorskii & Pakhomov
(107), the spin-wave theory of some rather complex systems shows at low
temperatures the same dependence of the magnetization upon the 3/2-
power of the temperature as was found by Bloch for monatomic cubic
structures. Ehrman (108), who calculated the properties of a gas of hard-
sphere fermions using a method devised by Brueckner, has obtained the
somewhat surprising result that the system becomes ferromagnetic at densi-
ties above a certain critical value; this conclusion has been verified by Morita
et al. (109). Several other theoretical developments are described below at
more appropriate places.

Neutron scattering.—Just as in the case of elastic vibrations, the mag-
netic excitations of solids can be detected by their effects on the scattering
of neutrons. A very general theory by Van Hove (110) shows that the scat-
tering cross-section in reciprocal space and energy is the Fourier transform
of a function in ordinary space and time which is the generalization of the
usual pair distribution function. Van Hove's approach has since proved use-
ful in a number of cases, the limitations so far being mostly those imposed
by the low neutron intensities encountered when energy analysis is at-
tempted.

Brockhouse (111) has measured the spectrum of neutrons inelastically
scattered from a magnetite crystal, and has attributed the energy losses to
the excitation of spin-waves; a spin-wave energy proportional to the square
of its wave-number seems to give a more reasonable value of the exchange
integral than does a linear dependence.

Near their Curie temperatures, magnetically-ordered systems are pre-
dicted by Van Hove to show striking scattering effects analogous to critical
opalescence in fluids. An approximate theory of these effects devised by
Elliott & Marshall (112) is in fairly good agreement with the observations
of Lowde (113) on the diffuse scattering by iron, especially close to the Curie
temperature. Similar results found by Wilkinson & Shull (114), including
small angle scattering from iron, nickel and Fe_3O_4, are due to the anticipated
long range correlations between spin directions, as shown by Gersch *et al.*
(115). An application of Van Hove's method to the scattering by a para-
magnetic substance has been made by Gennes (116).

Antiferromagnetic metals and alloys.—A number of rare earth metals and
alloys have shown signs of antiferromagnetic ordering at low temperatures.
At certain temperatures, anomalies appear in the susceptibilities of cerium,
neodymium and samarium [Lock (117); Behrendt *et al.* (118)], and of
cerium-lanthanum alloys [Roberts & Lock (119)], and heat-capacity maxima
appear at the same temperatures [(119); Parkinson & Roberts (120);
Roberts (121)]. In several cases, the susceptibility obeys a Curie-Weiss law

at high temperatures, the Curie constants being about right for the corresponding free trivalent ions, as if the 4f electrons were nearly as well shielded in the metals as they are in more dilute salts.

The face-centered cubic alloys of manganese with small amounts of copper (metastable γ-phase) have been known for some time to transform martensitically to a tetragonal structure. It has now been demonstrated that they simultaneously become antiferromagnetic [Bacon et al. (122); Meneghetti & Sidhu (123)].

At the opposite side of the copper-manganese system, unusual magnetic and electrical properties appear at low temperatures, even at very low manganese concentrations [Owen et al. (124); Gorter et al. (125); Schmitt & Jacobs (102, 126); Owen et al. (127); Sugawara (128); Lugt et al. (129)]. The alloys show susceptibility anomalies and hysteresis, resistance minima and maxima, pronounced magnetoresistance, and broadened resonances of the electron and Cu nuclear spin. It was at first thought (124) that an important role was played by indirect coupling of the magnetic ions through polarization of the conduction electrons. However, Hart (130) has pointed out, and Yosida (131) has verified by a perturbation calculation, that such a mechanism can give only short range coupling. The fact that the Cu nuclear resonance is hardly shifted is thus explained, but some strong Mn-Mn coupling is still required to account for the diffusely cooperative behavior.

Antiferromagnetic insulators.—The antiferromagnetic oxides MnO, FeO, CoO and NiO present an interesting structural problem. At high temperatures, all are isomorphous with NaCl, but on cooling through their Néel temperatures they undergo small distortions from cubic to tetragonal or rhombohedral symmetry. The early neutron diffraction studies have been repeated by Roth (132), who finds that some of the older magnetic structures must be revised, and also that a wider class of spin arrangements may have to be considered. A serious attempt to account for the spin structures and lattice distortions on the basis of a crystal-field approach has been made by Kanamori (133), with results in encouragingly good agreement with experiment. Keffer & O'Sullivan (134) conclude, in agreement with Kanamori, that the magnetic dipolar energy is the dominant term in the anisotropy of MnO. The three crystalline forms of MnS present structural problems somewhat like those of the oxides just discussed; Corliss et al. (135) have determined their spin arrangements, which are consistent with a superexchange model. Their magnetic properties can be accounted for rather well by the Ising model [Wojtowicz (136)].

A number of resonance investigations have given very detailed and precise information about magnetic interactions in antiferromagnetic MnF_2 and related compounds. The very large shift of the F^{19} nuclear resonance frequency in the paramagnetic state, observed by Shulman & Jaccarino (137), has been attributed by them to the partly covalent character of the Mn—F bond; the fluorine nucleus is thus subjected to the magnetic field of an unpaired electron which is polarized by the magnetic Mn^+ ion. The resonance

frequency shift is a direct measure of the amount of covalency, i.e., of the strength of the superexchange. Similar effects have been observed in other fluorides by Jaccarino *et al.* (138) and by Baker & Hayes (139); resonance methods have also been used to study exchange interactions in ammonium chloroiridate [Griffiths *et al.* (140)]. Below the Néel temperature of MnF_2, the magnetic ordering produces a very high internal field and correspondingly high nuclear resonance frequency. Jaccarino & Shulman (141) have observed this resonance frequency, which is proportional to the sublattice magnetization with a high degree of accuracy; the temperature variation is not in accord with spin-wave theory. Finally, antiferromagnetic resonance can give values of the product $H_E H_A$ (H_E is the exchange field, H_A the anisotropy field), as has been shown by Johnson & Nethercot (142) and Foner (143) for MnF_2, and by Dayhoff (144) for Cr_2O_3. The results are in good agreement with the Keffer-Kittel theory, based on a two sublattice, molecular field model.

The heat capacities of a series of nickel-zinc ferrospinels have been measured by Westrum & Grimes (145) to search for transitions between ferro- or antiferromagnetic states and "intermediate" triangular arrangements, as predicted by Yafet & Kittel, but without success; only one anomaly at most appears, probably a direct transition from the antiferromagnetic to the paramagnetic state.

Ferromagnetic domains.—Kittel & Galt (146) have reviewed this field quite recently, so that only a few late developments need be mentioned.

Coleman & Scott (147) have observed that the domain patterns on single-crystal iron whiskers are particularly simple in the unmagnetized state. A new technique for observation of domains has been applied to cobalt by Blackman & Grünbaum (148). In this method, a fine electron beam passing nearly parallel to the crystal surface is deflected by the leakage flux, and the patterns produced enable estimation of the domain size and flux distribution near the surface.

The motion of domain walls in iron is slowed to some extent by the presence of carbon and nitrogen atoms, whose energy in their octahedral holes depends on the local magnetization. The theory of this effect (developed by Néel) and the experimental results have been reviewed by Schreiber (149). Aside from its intrinsic interest, the effect can be used to measure the diffusion of carbon and nitrogen at low concentrations and temperatures, as shown by Brissonneau (150) and Bosman *et al.* (151). The activation energy for nitrogen diffusion found by the latter is in excellent agreement with that from anelastic measurements, but Brissonneau's value for carbon differs from the anelasticity result.

Miscellaneous theories.—Schlömann (152) has discussed the infrared absorption of ferrimagnetics, using the Kramers-Kronig dispersion relations, and has, among other things, suggested a possible method of detection of high frequency resonances by means of the magneto-optical Kerr effect. Gourary (153) has generalized the Kramers-Kronig relations to the case of

tensor susceptibility. A general tensor theory of magnetic rotatory power has been given by Le Corre (154).

A comprehensive review of the microwave properties of solids has been written by Bagguley & Owen (155).

DIFFUSION

As an experimental science, the measurement of diffusion coefficients in crystals has continued to flourish, but the data which accumulate appear to be understandable at best at the phenomenological level. In no case does it seem that a unique microscopic model has been established, although certain mechanisms can occasionally be eliminated by qualitative or semiquantitative arguments.

The possibility that successive jumps of a moving atom might be correlated was first considered by Bardeen & Herring (156). More recently the question has been treated theoretically by Compaan & Haven (157), who have calculated the correlation factor for several systems, assuming a vacancy mechanism; both analytical and analogue computations were used. [See also LeClaire & Lidiard (158)]. The diffusion coefficient of Ag in AgBr measured by Friauf (159) is markedly smaller than that calculated from the electrical conductivity, and the ratio can be satisfactorily accounted for by a mechanism involving two modes of interstitial motion including correlation effects.

The rates of diffusion of Cu and Zn in β-brass (approximately CuZn) have been measured by Kuper *et al.* (160) over a temperature range including the order-disorder transition. Only in the disordered state were simple Arrhenius laws followed, but the diffusion coefficient of Zn could be calculated over the entire interval from a simple elastic model. The fact that D_{Cu} and D_{Zn} do not become equal as perfect order is approached was adduced as evidence against a vacancy mechanism [see also Slifkin & Tomizuka (161)], but this conclusion was based on an incorrect theoretical analysis, as pointed out by Lidiard (162). The same criticism applies in part, at least, to the conclusions drawn by Eisen & Birchenall (163) from their measurements on InSb and GaSb.

In α-brass, the activation energy of the so-called "order peak" of the internal friction is closer to that for diffusion of Zn in a chemical gradient than it is to the energies for tracer diffusion of Zn or Cu; therefore, Hino *et al.* (164) conclude that this peak is associated with the motion of a cluster of Zn atoms, as has been assumed previously. Similarly, two of the internal friction peaks in β-brass have been associated by Clarebrough (165) with the stress-induced reorientation of Zn—Zn and Cu—Cu pairs; some of the evidence for this conclusion may have to be reassessed in the light of the later diffusion measurements (160).

Measurements made by Reynolds *et al.* (166) of diffusion in Au-Ni solid solutions both with and without a large composition gradient, combined with thermodynamic data for this system, support the Darken equation and

the idea that the "driving force" is more accurately the gradient of the chemical potential than that of the concentration.

The rates of self-diffusion of both anions and cations in six alkali halides show regularities [Laurent & Bénard (167)] which can be correlated with the ionic radii and with the plastic strengths and melting temperatures of the salts. Striking effects of the crystal structure on diffusion rates have been demonstrated for the three forms of AgI by Jordan & Pochon (168).

Classical reaction-rate theory predicts an effect of isotopic mass on diffusion rate in solids [Vineyard (169)] in disagreement with the experimental results of Lazarus & Okkerse (170) for Fe diffusion in Ag, but these results appear to be dubious. The self-diffusion of Ag is decreased by addition of Pd [Nachtrieb *et al.* (171)], contrary to the usual behavior; the latter is discussed by Hart *et al.* (172).

The rate of self-diffusion in solid CH_4 has been calculated from the temperature variation of the proton resonance line width by Waugh (173). A technique for measuring simultaneously the lattice and grain boundary diffusion coefficients from changes in total surface radioactivity has been described by Borisov *et al.* (174). [See also Condit & Birchenall (175).] Experimental methods are discussed by Jost (176). [See also Brissonneau (150) and Bosman *et al.* (151).] Various papers in the field of diffusion were presented at a conference at Eindhoven in 1956 [Fast *et al.* (177)].

IMPERFECTIONS

Dislocations.—It is to be expected that the new techniques for direct observation of single dislocation lines will stimulate the development of this field, while diminishing the rather *ad hoc* character of much of its theory. These developments are described in the first part of the proceedings of a recent conference [Fisher *et al.* (178)]. In more recent publications by Whelan & Hirsch [(179), and references given there] transmission electron microscopy has revealed, among other things, the existence in stainless steel of "extended dislocations" (two partial dislocations separated by a stacking fault). In a series of papers, Amelinckx and co-workers have demonstrated that dislocation lines have frequently a spiral form (180), and have suggested that such configurations may account for the spiral etch figures often seen on crystal surfaces (181). [See also Ellis (182); Pfann & Vogel (183); and Kikuchi & Denda (184).] Spiral dislocations may provide another mechanism for dislocation multiplication in growth from the melt (185) and for the growth of whiskers (186). Weertman (187) has shown that the spiral form is the equilibrium form of a dislocation line under certain conditions.

A promising technique has been developed by Hashimoto & Uyeda (188), Pashley *et al.* (189), and Bassett & Menter (189a), who have detected individual dislocation lines by "*moiré* patterns" in electron micrographs. These patterns were produced by interference between waves transmitted through two structures of identical period rotated relatively by a small angle (188), or through two structures of slightly different periods (189), giving in either case a considerably magnified image of the dislocation line.

Point defects (*exclusive of color centers*).—Kanzaki (190) has calculated the energies of a substitutional defect and of a vacancy in argon, using a method applicable to face-centered cubic (f.c.c.) structures generally. He also predicts that the diffuse x-ray scattering may have a shape in reciprocal space which is ellipsoidal (pairs of vacancies) or lemniscate (isolated defects). A similar result was also obtained for isolated defects in diamond structures by Yomosa & Nagamiya (191). Tucker & Senio (192) found experimentally an ellipsoidal distribution of the scattering from irradiated diamond. Sampson & Tucker (193) conclude that although the Bragg maxima are shifted further in a finite crystal containing point defects than in an infinite medium, there is no effect of size on the intensity distribution, contrary to calculations of Eshelby.

The additional electrical resistivity produced by quenching various metallic systems from high temperatures and its disappearance on subsequent isothermal annealing have been used to determine the heats of formation and heats of activation for motion of the corresponding defects (assumed to be vacancies). The results of Bradshaw & Pearson (194), Federighi & Gatto (195), and DeSorbo & Turnbull (196) for aluminum are all in fairly good agreement on the energies of formation (about 0.75 ev) and of migration (about 0.50 ev). Bradshaw & Pearson (197) find 0.95 ev and 0.68 ev for the corresponding quantities in gold, while Bauerle & Koehler (198) find 0.98 ev for the energy of formation. From the complex kinetic behavior described in the last paper, Koehler *et al.* (199) have derived rough values for the energies of formation and motion of divacancies. Jongenburger (200) has calculated energies of formation of vacancies in copper and gold from the anomalous expansions of these metals at high temperatures, but these must be considered as not very reliable because of uncertainties in the extrapolation of the "normal" expansions.

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NUCLEAR AND ELECTRON SPIN RESONANCE[1]

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A favorite pastime of resonance investigators since 1946 has been the modification of the original Bloch equations to describe additional experiments. Successively the theory has been generalized to encompass all weak-coupling nuclear resonance phenomena yet described [Bloch (1)]. It is probable that for a considerable period the emphasis will be on applying the general theory to special cases. It has long been recognized that spin resonance depends intimately upon relaxation processes, but with time there appears to be more emphasis upon studies directly concerned with relaxation. In the early days (1950) it appeared that one of the useful chemical applications of resonance was the interpretation of spectra in terms of electron densities. It is becoming apparent that conclusions from shielding or spin-spin coupling data must be drawn with care. Especially for protons, one finds appreciable shielding contributions from nonadjacent atoms. Likewise, spin-spin splittings do not always decrease in order of increasing interatomic distances. Interactions involving electron spins are receiving progressively more attention as the widespread occurrence and significance of fractional occupation of doublet and triplet states is recognized.

This reviewer would like to single out for commendation two papers whose authors have striven more for clarity than for elegance in the presentation of topics of general interest [Wilson (2); Feher (3)].

Reviews.—The third in a series of extensive reviews by the Oxford group deals with electron spin resonance (ESR) applications to intrinsic defects and impurities in solids, conduction electrons in metals, ferromagnetic, ferrimagnetic, antiferromagnetic, and cyclotron (diamagnetic) resonance [Bagguley & Owen (4)]. Interpretations of free radical spectra, dealing especially with hyperfine splitting, are summarized in two reviews [Weissman, Tuttle & De Boer (5); Fraenkel (6)]. Inferences about chemical bonding from nuclear resonance line width, shift and intensity are illustrated for various nuclei [Wertz (7)]. An excellent review describes optical-magnetic double resonance and "optical pumping" to selectively populate spin levels [Kastler (8)].

Relaxation theory.—A generalized treatment of relaxation by Bloch was summarized in Volume 8 of this series [Bloch (9); McConnell (10)]. (A less comprehensive treatment along similar lines has appeared [Vojta (11)].) In this theory the dominant part of the energy of the spin system was assumed to be independent of the time. A more general theory dispenses with this assumption, retaining the proviso that the system be weakly coupled to the

surroundings, which are assumed to be in thermal equilibrium. The coupling is considered weak if interactions produce effects which on a frequency scale are small compared to the inverse of the correlation time of the lattice and of $\hbar/kT$. This theory includes all results derived previously as special cases. The derivation of the first order linear differential equation for the Boltzmann distribution matrix is carried out in a form which is valid for any representation of the spin system. The expectation values of the spin functions are then obtainable from a system of differential equations. When the spin system is coupled to the molecular surroundings, there are terms involving relaxation and a correction of the spin energy. As a special case, one finds when the field is nearly constant that the distribution matrix becomes appropriate to thermal equilibrium at the instantaneous value of the dominant part of the spin energy. When applied to the case of a single nucleus of spin $\frac{1}{2}$, in a rotating magnetic field, the expectation value of the spin vector contains five distinct time constants, instead of the usual thermal time t_1 and the spin-spin time t_2. Steady-state solutions are given for the special cases: static field; vanishing transverse field; weak field near resonance; slowly rotating field [Bloch (1)].

A derivation of relaxation behavior without use of statistical arguments is intended to demonstrate the irreversibility of spin-lattice interaction [Seiden (12)]. Other treatments of relaxation processes are given for quadrupole mechanisms [Khutsishvili (13)], for the body-centered cubic lattice (quadrupole relaxation) [Das, Roy & Roy (14)], and for liquids, with various choices of the radial distribution function [Seiden (15)].

Applications of relaxation.—The most detailed study yet carried out in the three phases of a single substance was done with H_2, including in some cases HD and D_2. In gaseous H_2, frequent collisions eliminate the complex spectrum observed in molecular beams and arising from the rotational magnetic moment and spin-rotational interaction. Although one does not observe lines due to these effects, the modulation of spin-rotational and dipole-dipole interaction by collisions leads to thermal relaxation. Measurement of t_1 as a function of temperature, density, and ortho-H_2 concentration permit the calculation of an average time spent in a given rotational state under various conditions. The cross-section for collision leading to transition between rotational states, and effective in relaxation, gives a measure of the anisotropic part of the ortho-ortho and ortho-para interactions. The relaxation time in HD is long because one has no spin-rotational interaction in the ground state ($J=0$), and one can infer the mean time spent in the $J=1$ state from t_1 measurements. The behavior of liquid H_2 closely parallels that of the gas. Dipolar interaction between nuclei in the same molecule are modulated by effects which cause the molecule to rotate or reorient. Such motions are highly effective, while purely translational motion makes a negligible contribution to t_1. However, the reverse is true for HD. In solid H_2 near the melting point, self-diffusion is appreciable and relaxation occurs from reorientations of ortho-H_2. In HD the relaxation appears to result from H_2 impurity [Bloom (16)]. A theoretical study of H_2 and D_2 at temperatures

too low for appreciable self-diffusion indicates that relaxation is effected by intramolecular interactions which are modulated. When self-diffusion occurs, it makes an appreciable contribution at low frequencies. For D_2, spin exchange plays an important role in establishing thermal equilibrium [Moriya & Motizuki (17)].

A single temperature-independent correlation frequency is found to give an adequate account of relaxation times in CH_4. It is concluded that relaxation measurements do not distinguish between molecular reorientation and self-diffusion, while line-width data make this distinction possible [Waugh (18)]. Relaxation times in solid 1,2-dichloroethane range from 1 to 20 sec., and these values are correlated with internal motions [Linder (19)]. Relaxation times and line width changes are consistent with interpretations of two-phase behavior in polytetrafluoroethylene as arising from crystalline and amorphous regions [Wilson & Pake (20)].

When in an ionic solid one irradiates nucleus B with a strong r-f field H_1, the relaxation rate of a neighboring nucleus A is a maximum when $\omega_A = \gamma_B H_1$ [Hahn & Kaplan (21)]. This condition is derived on dipolar considerations, and it is predicted that the effect would disappear if the strong field were along a crystal axis [Hue & Seiden (22)].

Quadrupole relaxation appears to be responsible for wide proton or nitrogen lines in NH_3 and in unsymmetrical ammonium salts, while narrow lines are observed for tetrahedrally symmetrical NH_4^+ and $(CH_3)_4N^+$ ions [Ogg & Ray (23)].

Multiple thermal relaxation times.—"Relaxation spectroscopy" in ionic solutions permits the detection of regions differing in "amount of relaxation" by studying line broadening or shift and the reversal of magnetization with time. A well-defined group is constituted by those molecules for which the lifetime in the solvated state is close to the local relaxation time. Lifetimes for water protons immediately adjacent to diamagnetic trivalent ions are found to be about 10^{-2} sec. In dilute paramagnetic solutions, the lifetimes of protons range from 1 to 300 μsec. The effective size of the hydration envelope is one or two layers for dilute solutions and two to three layers for concentrated. Units of four layers radius and 5 msec. lifetime are thought to be "ice crystals" [Broersma (24)]. Relaxation rates of protons in ferric perchlorate solutions have been measured from pH 0 to 12 in order to establish the magnetic moments of various iron ions. $Fe(OH)_2^+$ and $Fe(OH)^{+2}$ both have the same moment as Fe^{+3}, while $Fe_2(OH)_2^{+4}$ is diamagnetic [Broersma (24)]. Relaxation (spin-lattice or spin-spin) has been treated as a Markoff process for the limiting cases of very slow or very rapid exchange. In a two-phase system one may give a description of relaxation for intermediate situations. For the water-silica gel system, t_1 data show a single-phase behavior, while previous work indicated a two-phase behavior for t_2. An estimate of the mean lifetime of water on the gel gives about 3 msec. [Zimmerman & Brittin (25)].

When the reciprocal relaxation times $1/t_1$ of protons in mesitylene $[C_6H_3(CH_3)_3]$ solutions are plotted against concentration, one has separate

straight lines for the ring and the methyl protons, corresponding to distinct relaxation times. The t_1 for each may be resolved into inter- and intramolecular contributions, the major effect for the ring protons coming from those on adjacent methyl groups [Reilly & Strombotne (26)]. Relaxation times of the high-temperature phases of liquid crystals are comparable with other isotropic systems. Just above the transition there is a decrease either of t_1 or t_2 for the systems studied. These changes come from the formation of groups of molecules which nucleate the oncoming transition. Restriction of motions alters correlation times and leads to changes of relaxation times [Runyan & Nolle (27)].

Paramagnetic effects.—In aqueous solutions of Mn^{+2} or Gd^{+3}, $t_1 = t_2$ for protons at low frequencies, but at 30 Mc., t_1 is much larger than t_2. For Mn^{+2} or Cr^{+3} one observes a decrease of t_1 with decreasing field, but not for Co^{+2} or for Nd^{+2}. No change of t_2 with field was observed [Nolle & Morgan (28)]. At high frequencies, as a result of attachment of a water molecule to an ion, a spin exchange interaction shortens t_1 appreciably, while affecting t_2 but little. As the frequency is diminished, t_1 is progressively reduced to approximate equality with t_2 at about 3 Mc. [Bloembergen (29)]. An unusual increase in signal-to-noise ratio for ferrocene $Fe(C_5H_5)_2$ in going from 190 to 110°K. is said to be due to shortening of t_1 by relaxation processes involving electron transfer [Holm & Ibers (30)].

In a multilevel system such as gadolinium ethyl sulfate with added cerium, one may study the apparent relaxation times (power saturation method) as a function of crystal orientation. Marked reduction in relaxation time occurs when a gadolinium transition coincides with one of cerium or with another Gd transition [Feher & Scovil (31)].

The thermal relaxation time in potassium ferrocyanide at 4°K. and in a field of 500 to 1000 gauss has the remarkably long value of 10^{-3} seconds [Haseda & Kanda (32)].

Proton times t_1 in antiferromagnetic $CuCl_2 \cdot 2H_2O$ were measured as a function of orientation, applied field and temperature. Thermal fluctuations of the moments of the copper ion occur predominantly in the direction of their time-average magnetic moment [Hardeman, *et al.* (33)].

Shielding calculations.—Magnitudes of chemical shifts have been computed by considering the currents induced by applied magnetic fields. Using atomic orbitals, current densities are calculated at a particular atom by replacing all other currents by point dipoles. Local paramagnetic currents may influence the resonance frequency markedly. In the series CH_4, NH_3, H_2O and HF, where the paramagnetic currents about the central atom nearly annul the effect of increasing electronegativity, there is little change in the proton frequency. While for other elements the circulation around a particular atom largely determines the chemical shift, for hydrogen the electron density is so low that distant circulations may give an appreciable contribution [Pople (34)]. When applying the Pople model to polycyclic hydrocarbons, one must take into account all possible paths [Hazato (35)]. In aro-

matic molecules, an attempt has been made to secure better agreement with experiment by splitting aromatic ring currents into parts above and below the rings [Waugh & Fessenden (36)]. Shielding has been studied for the protons in fused-ring systems which in a planar structure would be separated by less than the van der Waals diameter. The difference between the observed shielding and that calculated on the basis of circulating currents in adjacent rings is attributed to the steric effect [Reid (37)]. When the ring current concept is applied to the ions $C_5H_6^-$ and $C_7H_7^+$, the calculated shifts are in poor agreement with measured values [Leto, Cotton & Waugh (38)].

By extending Ramsey's theory for shielding in H_2 to more complex molecules, estimates have been made of the shielding at a given proton by remote nuclei. The long-range effects are expected to be significant in aromatic compounds and alkyl halides. Hence one cannot expect to obtain electron densities at given protons directly from their measured shielding [McConnell (39)].

A variational calculation is found to reproduce satisfactorily the observed shielding in H_2 and the hydrogen halides. Besides the interatomic distance and the bond character, the shielding depends on the number of electrons possessed by the atom attached to hydrogen [McGarvey (40)]. The validity of a previous calculation by variational methods has been questioned [Hornig & Hirschfelder (41); McGarvey (42)]. Another variational calculation gives the correct order of shielding as C_2H_4, C_2H_2, and CH_4, although all calculated values are high [Stephen (43)].

Inferences from shielding.—For the methyl halides at infinite dilution, the shifts are in the order of the Huggins electronegativities. Using the methyl halide shifts for the calibration of a scale, electronegativities were assigned in a series of compounds in which the hybridization of the C—X bond is nearly constant. [Allred & Rochow (44)]. Chemical shifts in m- and p-substituted fluorobenzenes are expressed by equations in terms of "inductive" and "resonance" (mesomeric) components of Hammett's σ-function [Taft (45)].

In $Ni(C_5H_5)_2$ the proton resonance is displaced by about one gauss to higher field, notwithstanding the presence of the paramagnetic atom. The explanation offered is that the unpaired electrons spend an appreciable fraction of their time on the rings, where π-σ configuration interaction gives an electron spin polarization at the protons opposite to the net polarization of the molecule. If the electrons are localized on the rings half the time, the calculated shielding agrees with experiment [McConnell & Holm (46)].

The explanation of displacement of proton frequency by paramagnetic ions in terms of "anisotropy of the g-shift" cannot be correct for Mn^{+2} or Gd^{+3} ions. Rather, it is suggested that for all paramagnetic ions the effect is to be attributed to a spin exchange interaction [Bloembergen (47)].

The resonant field of hydrogen in Ta or V is very close to that of water. The small shift is interpreted as indicating electron pairing at the hydrogen atoms [Oriani, McCliment & Youngblood (48)].

The unusually large resonance shifts between various trivalent cobalt complexes and their large variations with temperature are related to variations in ligand field splitting, the latter being measurable by optical absorption studies [Griffith & Orgel (49)]. Applying these concepts, an approximately linear relation between resonance frequency and wavelength of the lowest-frequency optical band is found. In the two cases investigated, the temperature-dependence is that predicted [Freeman, Murray & Richards (50)].

Fluorine shieldings in a series of partly-fluorinated aliphatic compounds appear to fall into well-defined groups. The greater shielding of CF_3 in $(CF_3)_3CF$ as compared with $(CF_3)_4C$ is not yet explained [Muller, Lauterbur & Svatos (51)].

"$GaCl_2$" is found to give two Ga lines, in agreement with the formula $Ga(GaCl_4)$ obtained by other methods [Richards (52)].

Appreciable shifts are found between protons in equatorial and axial positions in acetylated carbohydrates. Similar shifts are found for the protons in the acetoxy groups [Lemieux et al. (53)].

Ribonuclease is thus far the only protein reported to show multiple resonance lines. [Saunders, Wishnia & Kirkwood (54)]. A suggested interpretation of the four observed lines has been made on the basis of amino acid studies [Jardetzky & Jardetzky (55); Takeda & Jardetzky (56)].

Structural information has been obtained for P_4S_3, $P_4O_6S_3$, phosphite esters and salts, as well as for other phosphorus oxy-ions [Callis et al. (57)].

Of the various possible species of complex fluoride ions of aluminum in solution, one observes separate fluorine resonance lines for AlF_2^{-1} and AlF^{-2} with intensities in the expected ratios [Connick & Poulson (58)].

Observation of the dispersion signal of ^{13}C in natural abundance has permitted shielding and spin-spin coupling to be measured in about 100 compounds. The range of variation of shielding is about half that in ^{14}N or ^{17}O, where second-order paramagnetism is marked [Lauterbur (59); Holm (60)].

Separate resonance lines for the rotational isomers of alkyl nitrites, RONO, allow cis:trans ratios to be determined. Steric considerations cause the trans isomer to be the stable form for the isopropyl and isobutyl nitrites [Phillips, Looney & Spaeth (61)]. The trans form is also the more stable for CH_3ONO [Piette, Ray & Ogg (62)]. Temperature-dependence studies of the cis and trans lines of nitrosamines give ΔH values for interconversion of 1 to 23 kcal. The resonance study has aided in the interpretation of infrared spectra [Looney, Phillips & Reilly (63)].

Solvent interactions.—A large number of compounds appear to obey the relation $H = H_{appl}S(1 - 2.6K)$, where H represents the field at a bare proton, H_{appl} is the applied field, S is the shielding factor and K is the volume susceptibility of the sample. When this relation is obeyed for a solution, one may safely use one line as an internal reference and obtain directly the separations at infinite dilution. When aromatic compounds are present, the equation does not apply, and one obtains such anomalous effects as relative shifts of

multiple lines in a compound and different shifts at infinite dilution upon changing solvents. These effects are not well understood [Bothner-By & Glick (64)].

Resonance of water protons in solution increases in the order: Pure water; solutions in $CHCl_3$, CCl_4, C_6H_6; water vapor. The dipole moment of an isolated water molecule is assumed to increase when surrounded by neighbors which are polarizable or which have a dipole moment [Ogg (65); Ogg & Diehl (66)]. Extending this concept to alcohols, one finds the OH line of EtOH in C_6H_6 to occur at a higher field than for the CH_2 protons, suggesting that the effect of electronegativity of an adjacent bound oxygen is less than that of electrostatically induced polarization in the liquid [Diehl (67)].

Chloroform appears to form 1:1 complexes with benzene, its threefold axis coinciding with the sixfold axis of the ring [Reeves & Schneider (68)]. It also forms similar complexes with such molecules as Et_2O or $CHCl_3$, the shift being interpreted as a measure of hydrogen bonding [Korinek & Schneider (69)]. The complexes between BF_3 and a mixture of alcohols show well-resolved fluorine lines at sufficiently low temperature. When insufficient BF_3 is present to complex all the alcohol molecules, the relative intensities of the lines give a measure of the stability of the complexes. The stability decreases as one goes from water to alcohols of increasing molecular weight [Diehl & Ogg (70)].

Keto-enol equilibria should be expected to shift between one polar solvent and another. Such displacements can be predicted on the basis of hydrogen bonding considerations [Reeves (71)].

Other chemical shift studies include: Fluoronaphthalenes [Isobe, Inukai & Ito (72)]; fluoromethyl groups [Tiers (73)]; trivalent phosphorus compounds [Parks (74)]; ^{17}O in H_2O_2 [Lüscher (75)]; nitro compounds [Ray & Ogg (76)].

Chemical exchange.—Proton transfer between methylamine and methylammonium ion appears to occur in two ways. Besides direct transfer from $CH_3NH_3^+$ to CH_3NH_2 the transfer may proceed via water molecules of solvation. For calculation of rate constants, it was necessary to observe proton line changes with pH for CH_3, NH_3^+ and H_2O lines [Grunwald, Loewenstein & Meiboom (77)]. A similar study has been carried on for $(CH_3)_2NH_2^+$ and $(CH_3)_3NH^+$ [Loewenstein & Meiboom (78)]. Proton shifts relative to $(CH_3)_4N^+$ for $CH_3NH_3^+$, $(CH_3)_2NH_2^+$, and $(CH_3)_3NH^+$ are linear functions of mole fraction if the nature of the solvent is unchanged [Grunwald, Loewenstein & Meiboom (79)].

A further study has been made of the conditions under which nuclear resonance line width measurements may lead to a value for the rate of electron transfer between para- and diamagnetic forms of a given substance [McConnell & Berger (80)].

The marked temperature dependence of the F resonance in ClF_3 is ascribed to fluorine exchange, presumed to occur through a dimer intermediate [Muetterties & Phillips (81)].

Exchange of deuterium between B_2D_6 and B_5H_9 is found to take place preferentially at the terminal hydrogen positions [Koski, Kaufman & Lauterbur (82)].

Other exchange studies include the systems: $H_2SO_4 - H_2O$ [Hood & Reilly (83)]; acetic anhydride-water or alcohols [Bhar & Forsling (84); Bhar (85)].

Spin-spin interactions.—The progressive decrease in spin-spin coupling constants normally expected with increasing number of intervening bonds is found by a calculation using atomic orbitals. The correct behavior is not found when using molecular orbitals [Aihara (86)].

Deviations from perfect pairing occur in the valence bond treatment of polyatomic molecules, and it is suggested that spin-spin interactions are a measure of such deviation [Karplus, Anderson, Farrar & Gutowsky (87)].

Magnitudes of hyperfine splitting in organic free radicals are used in esti- mating the contribution of π-electrons to spin-spin splitting. The latter is proportional to $(Q\eta_{ij})^2/\Delta E$, where Q relates proton hyperfine splitting to un- paired electron density on the adjacent carbon, ΔE is an effective electronic excitation energy and η_{ij} is the bond order between positions i and j in the aromatic ring. Magnitudes of bond orders and coupling constants are tabu- lated for all i and j in benzene and naphthalene. The maximum splitting contribution is about 1 c.p.s. [McConnell (88)].

The procedure for setting up and solving equations for spin-spin coupling in a molecule of chosen symmetry is explained in detailed and lucid fashion. Group theory is applied to set up spin functions and factor the secular equa- tion, selection rules are determined, and intensities calculated. The procedure is illustrated for 1,3,5-trifluorobenzene [Wilson (89)]. A detailed study of fluorobenzene has led to values for coupling constants. Allowed transitions and relative intensities for an unsymmetrical three-spin system are tabulated. The proton-proton constants are of the same sign for ortho and meta posi- tions but of opposite sign for ortho and para positions. The couplings are not readily separated into primarily π or σ interactions [Gutowsky, Holm, Saika & Williams (90)]. Procedures have been enumerated in detail for the analysis of a four-spin system having coupling constants of the same order of magnitude as the chemical shifts (A_2B_2 case). It is applied to naphthalene (each ring assumed independent), o-dichlorobenzene and 1-chloro-2-bromo- ethane [Pople, Schneider & Bernstein (91); Bernstein & Schneider (92)]. The use of a high-speed computer has permitted an investigation of the effect of changes in the relative magnitudes of the chemical shift and of each of the four coupling parameters in the A_2B_2 case. With 133 combinations of param- eters, one can rapidly make approximate assignments to a new spectrum [Schwabacher & Wertz (93)]. As an aid in the assignment of chemical shifts and coupling constants for a complicated spectrum, a method of multiplet moments has been devised. Combinations of coupling constants, rather than individual values are obtained [Anderson & McConnell (94)].

Substituted ethanes of the type RF_2C—$CXYZ$ give multiple fluorine resonance lines [Drysdale & Phillips (95)]. While restricted rotation could

give this result, one should expect it even with rapid reorientation unless the residence time in each of the principal conformations is equal [Nair & Roberts (96); Gutowsky *et al.* (90)]. Resolved proton spin-spin interactions are observed for such compounds as CH_2BrCH_2OH and $C_6H_5CH_2Br$ [Graham & Waugh (97)].

The ^{11}B spectrum of B_5H_{11} has been assigned on the basis of the known structure, but only partial interpretation of the proton spectrum was made [Schaeffer, Shoolery & Jones (98)].

Substitution of a perfluoroalkyl group for one fluorine in SF_6 is found to leave the remaining fluorine atoms in a square pyramid. After a further substitution, the remaining four lie in a plane unless a ring was formed. In the latter case, the C—S—C bond angle is about $90°$, so that one has two nonequivalent pairs. No spin-spin splitting appears to be transmitted through the C—S bond [Muller, Lauterbur & Svatos (99)].

A fluorine doublet is observed in F_2POOH at 37 gauss with the same splitting as at 6365 gauss [Roux & Béné (100)]. It had previously been reported that there was only a single line at 200 gauss [Quinn & Brown (101)].

If in succession one traverses resolved resonances A and B (e.g. spin-spin multiplet components), the amplitude of the latter will be reduced if a spin transfer occurs by exchange or internal rotation. The reduction is dependent upon the magnitude of H_1 and the sweep rate [McConnell & Thompson (102)].

Unusual spin-spin splittings.—Coupling between F and H across a cyclobutene ring appears to be greater than between adjacent positions [Sharts & Roberts (103)]. Strong coupling occurs when fluorine atoms are separated by C—N—C bonds, although in CF_3CF_2COOH one observes only a single line [Muller, Lauterbur & Svatos (51)]. Coupling of ^{207}Pb with CH_3 protons is greater than with CH_2 in $PbEt_4$ [Baker (105)].

Another example of double-quantum transitions has been reported, this time in EtOH. These lines appear when the r-f field H_1 exceeds the optimum value for single-quantum transitions [Kaplan & Meiboom (106)].

Solid structures.—The configuration of fumarate formed from malate in the presence of fumarase is indicated by solid line studies as *cis*. The hydrolysis in D_2O yields a structure in which most of the intramolecular dipole broadening of the proton line comes from the CHD—CH portion of the molecule [Farrar, Gutowsky, Alberty & Miller (107)]. Other studies on solids include: CaF_2 [Bruce (108)]; tetrahalogen methanes [Takeda & Gutowsky (109)]; halogenated ethanes [Gutowsky & Takeda (110)]; guanidinium aluminum sulfate hexahydrate [McCall (111); Spence & Muller (112)]; polymers [Nishioka, Komatsu & Kakiuchi (113); Fuschillo & Sauer (114); Fujiwara, Amamiya & Shinohara (115); Kusomoto (116)]; paradichlorobenzene [Buyle-Bodin (117)].

Quadrupole splitting.—By applying stresses to crystals of InSb or GaSb, which had so highly ordered a structure that electric field gradients could not be detected, the symmetry could be reversibly altered. From observation of

broadening of ^{115}In lines, strains of less than 10^{-4} could be detected and electric field gradients evaluated. The effects are 70-fold greater than would result from displacement of charges alone [Shulman, Wyluda & Anderson (118)].

Motions in solids.—The heights of potential barriers to rotation of CH_3, NH_3^+ and NH_2 groups as well as C_6H_6 and H_2O molecules have been calculated. Their dependence upon effective moment of inertia I_{eff} for tunnelling and for classical rotation indicates that the former may be ignored except for protons. Tunnelling falls off more slowly with increasing barrier height and has a smaller temperature dependence than classical rotation. I_{eff} is given for correlated and uncorrelated motions and for rolling motions [Das (119)]. Calculations have also been made for a two-proton system free to rotate about an axis [Bloembergen (120)].

Broad and narrow line components in polyethylene were originally ascribed to crystalline and amorphous regions. Comparison with other methods of establishing crystallinity has led some workers to the conclusion that these lines reflect the extent of internal motions [Rempel *et al.* (121)].

Ferrocene retains reorientational motions to a remarkable extent even at low temperatures. However, dibenzene chromium with a similar structure shows appreciable loss of motion at 77°K. [Mulay, Rochow & Fischer (122)].

Methane adsorbed on TiO_2 appears to show both broad and narrow line components. The latter are ascribed to a surface diffusion [Fuschillo & Renton (123)].

A study of liquid crystals gives evidence for preferred orientation of the long axis in the magnetic field direction [Lippmann & Weber (124)].

Other studies of internal motions include: Cyclohexanol [Averbuch (125)]; natural rubber [Gutowsky *et al.* (126)]; hexamethyldisilanes [Yukitoshi *et al.* (127)]; various polymers [Yoshida *et al.* (128); Odajima, Sohma & Koike (129)].

Transient effects.—A remarkable set of five echoes has been obtained in solid KI, following initial pulses of 90 and 35 degrees. Three of the echoes are of simple bell shape and correspond to $\Delta m = \pm 1$ transitions, while the other two have the form of the derivative of an absorption curve and arise for $|\Delta m| > 1$. These echoes are in accord with theory for a solid system in which there is appreciable quadrupole interaction if the r-f field magnitude is large compared with the quadrupole interaction measured in gauss [Solomon (130)]. The number of observable echoes from n pulses is equal to $1/4(3^n - 2n - 1)$. This expression has been verified experimentally up to $n = 5$, with proper choice of pulse angle and separation. The three-pulse spin echo system is studied with a view to choosing such pulse angles that magnetic field fluctuations lead to minimum reduction in amplitude of echoes [Ghose, Ghosh & Roy (131)].

Spin echoes of water protons in an ionic solution undergoing alternating current electrolysis show intensity fluctuations [Geissler & Pfeifer (132)].

Spin echoes are cited as an example illustrating the concept of irreversi-

bility. The entropy defined in terms of information increases if information is lost in storage [Rothstein (133)].

The pronounced beats in free-precession decay observed for solids are interpreted as the Fourier transform of the steady-state line shape. It is shown that the line shape for an ordered rigid lattice is not Gaussian [Lowe & Norberg (134)]. Beats which are due to spin-spin coupling permit one to determine the mean value of coupling constants [Elliott & Schumacher (135)].

Other studies of transient effects include: Signals in flowing liquids [Antonowicz (136)]; line shapes in rapid passage (Kurochkin (137)]; first harmonic component of a line [Shpiegel, Raiser & Miae (138); shapes of dispersion signals [Ievskaya (139)].

Spin temperature.—An intriguing group of "nuclear calorimetry" experiments performed at Saclay is presented as a substantiation of the concept of spin temperature. It has been known for a long time that relaxation times in low field (e.g., the earth's field) may be much shorter than at high fields. Thus, while in their resonant fields corresponding to 8 Mc., ^{7}Li and ^{19}F have t_1 respectively equal to about 4.5 min. and 1.4 min., their common value of t_1 in the earth's field is about 6 sec. The polarizations of both are observed after they have been taken from a strong field to the earth's field and then returned in a time short compared with t_1. While the energy states of Li and F are widely separated in the strong field, in a weak field they will come together and find a common spin temperature in a short time. If one nucleus is originally saturated, it will acquire the sign of the polarization of the other nucleus, which may previously have had the population of its levels inverted. When both are in a state of negative spin temperature before mixing, their temperature remains negative afterwards. This attainment of a common spin temperature makes it possible to polarize rapidly a nucleus of long relaxation time if it is periodically withdrawn from a strong field in thermal contact with another nucleus of much shorter t_1. Thus, Cs in CsCl was polarized much more rapidly by frequent withdrawals from a strong field used to polarize chloride ions than if it had remained in the field [Abragam & Proctor (140)]. On the other hand, the concept of spin temperature has been criticized as likely to lead to ambiguities. The use of chemical potentials is advocated to describe spin distributions, using a single temperature for spin systems and lattice. Spin interactions are treated as chemical reactions and conditions of equilibrium are formulated. This approach allows a simple derivation of an equation for the nuclear polarization resulting from saturation of the electron spin system [Desloge & Barker (141)]. No doubt this topic will continue to be a lively one in the near future.

Enhanced polarization effects.—If nuclear spins are coupled to an electronic spin system which is being saturated, there is an enhancement of the nuclear polarization (Overhauser effect). If one uses the free radical ion $(SO_3)_2NO^{-2}$ in water solution with only the earth's field to produce polarization, the nuclear resonance signal from the protons is phenomenally low in noise. Upon increasing the r-f power at 56 Mc. (corresponding to electron

spin transitions between hyperfine levels having a large zero-field splitting), the proton signal is observed to decrease to zero, followed by an increased signal of the opposite phase. The expectation value of the nuclear polarization is calculated as $8/27(\Omega/\omega)S_0$, where Ω and ω are the hyperfine separation and the electron resonance frequencies respectively, while S_0 is the steady-state electronic polarization. This is a much greater enhancement of polarization than for the ordinary high-field Overhauser effect. Since energy is given to the r-f field, the effect has been used to construct a maser [Abragam, Combrisson & Solomon (142)].

In paramagnetic systems having a sufficiently large quadrupole interaction or nondiagonal hyperfine structure terms, nuclear polarization may be achieved by saturation of forbidden transitions $\Delta(m+M) = 0$, giving $2I$ lines [Jeffries (143)]. This effect has been demonstrated by γ-ray anisotropy for ^{60}Co and has also helped to establish the spin of ^{76}As ($I = 2$) [Abraham, Kedzie & Jeffries (144); Pipkin & Culvahouse (145)].

A study of various electron spin relaxation processes has shown that a transient analog of the Overhauser effect may produce polarization in silicon containing P, As, or Sb [Pines, Bardeen & Slichter (146)]. Additional relaxation mechanisms have been studied, but they are not as effective as the Pines-Bardeen-Slichter mechanism [Abrahams (147)].

When one set of nuclei in a rigid solid is saturated, the polarization of other nuclear types is reduced. If motion occurs, the magnitude of the polarization agrees with experiment for PH_4I [Little (148)].

Metals.—Studies of resonance in Cu—Mn alloys had shown that the effects of the Mn upon the Knight shift, ESR shift, relaxation time of d-electrons and antiferromagnetism are less than those expected for Mn^{+2} ions with s-d exchange coupling [Owen, Browne, Knight & Kittel (150); van der Lugt, Poulis, Hardeman & Hass (151)]. Line width contributions from dipolar and indirect exchange coupling as well as the temperature and field dependence reproduce the experimental data reasonably well [Behringer (152)]. Susceptibility studies show that the average spin lies between 2 and 5/2, while the ESR g-value is near 2 and shows little anisotropy. The behavior is consistent with strong direct and superexchange interactions, but the data do not establish conclusively the presence or absence of 4s electrons for Mn. Antiferromagnetic resonance is observed, although there are strong ferromagnetic interactions [Owen *et al.* (153)].

The Knight shift is reduced in going from the normal to the superconducting state of Hg. The shift continues to diminish from the critical temperature to 1.2°K. [Reif (154)]. For Al, the increased relaxation rate upon entering the superconducting state is in accord with a one-electron energy gap model, but is inconsistent with a two-fluid model [Hebel & Slichter (155)].

In metals with spin $I \geq 1$, it is possible for anisotropic hyperfine interaction with conduction electrons and quadrupole interaction to be as effective as the contact interaction [Mitchell (156)].

The polarization of nuclei in metals under ESR conditions is found theoretically to vary slowly with depth, permitting the use of thick foils if a

large field H_1 is used. The mean distance traveled by an electron between collisions in which spin reversal occurs is 10^{-2} to 1 cm. Metallic films show a selective transparency in ESR, with the transmitted wave circularly polarized if H_z is normal to the film [Azbel, Gerasimenko & Lifschitz (157)].

The effect of eddy currents in metals is found to give a displacement of the apparent center of the resonance in the direction opposite to the Knight shift and the apparent intensity is altered. There is a marked dependence upon size and shape of samples [Chapman, Rhodes & Seymour (158)].

Estimates of order of magnitude of spin-orbit contributions to the ESR g-factor of metals have been given without making numerical calculations for specific metals [Yafet (159)].

Shifts, line widths and t_1 for Cu and Al are given as a function of temperature for soild solutions of transition metals in these metals [Sugawara (160)]. Line widths have been studied for impure Li as a function of particle size [Garif'yanov (161)]. The temperature dependence of the Overhauser effect has also been studied in Li [Bekeshko & Kondorskii (162)]. Knight shift, line width and shape, and t_1 have been investigated in Cd. The asymmetry in the p-character of conduction electrons is estimated [Masuda (163)].

ESR of free radicals.—It is convenient to treat unpaired electron distributions in terms of a "spin density" defined in such a way that it has a value unity at the nucleus of a hydrogen atom. A knowledge of spin densities at various carbon atoms permits an interpretation of hyperfine spectra, since the splittings for protons are proportional to the spin densities at the adjacent carbon atoms. Until recently it had been assumed that any magnetic polarization in a free radical was of the same sense as the macroscopic polarization. However, both molecular orbital and valence bond approaches may give structures in which there are some atoms with inverted polarization. In molecular orbital theory, negative densities can arise from π-π configuration interaction. As an example of the use of valence bond theory, one may assign a negative spin density of 1/3 to the central carbon atom on an allyl radical, with positive spin densities of 2/3 on the terminal atoms. Using valence bond theory, one need not resort to ionic structures to obtain negative densities. Since the net spin density for a monoradical totals unity, one can have much larger densities on an atom than if the minimum density were zero. This may lead to an unusually extended spectrum as in the case of the perinaphthenyl radical mentioned later. Triphenylmethyl presumably has appreciable negative spin density at the six meta carbon atoms, having a magnitude 35 per cent of the total density on the ortho and para carbon atoms [McConnell & Chesnut (164)].

Valence bond calculations of the positions and intensities of the hyperfine spectrum of the triphenylmethyl radical give twenty-one groups, closely resembling the experimental spectrum [Brovetto & Ferroni (165); Jarrett & Sloan (166)]. Their mechanism assumed for the hyperfine coupling between electrons and protons has been questioned [McConnell & Chesnut (164)]. The assumption of large splitting by meta protons and zero splitting by para is highly unlikely [Lupinski (167)]. Empirically it has been noted that the hy-

perfine coupling constant for a given proton is equal to the unpaired electron density at the adjacent carbon atom multiplied by a constant of magnitude about 30 gauss. [McConnell (168)]. This expression may be derived on the Dirac vector model if one assumes that all σ-π excited states have approximately the same excitation energy [McConnell (169)].

Experimental line shapes for anions of anthracene, naphthalene, and biphenyl are satisfactorily reproduced by obtaining π-electron charge densities and assuming that proton hyperfine splitting constants are directly proportional to these [De Boer (170)].

It is well known that a resolved hyperfine spectrum of a free radical can be observed only if the exchange interaction J in frequency units is less than the separation A of hyperfine components. When $J \gg A$, only a single narrow line is observed, as in solid free radicals. As J is allowed to decrease to approximate equality with A, the line broadens to a maximum value. Further reduction in J leads to resolution of hyperfine components and their narrowing to some limiting width [Pake, Weissman & Townsend (171)]. This exchange is illustrated later in the case of the naphthenyl ion and the 4.4'-oxy-*bis*-triphenylmethyl radical. The detailed calculation of exchange effects has been undertaken on the basis of a theory of Kubo & Tomita (172). Dipole interactions are also taken into account [Kivelson (173)].

Anthracene, tetracene and perylene in concentrated H_2SO_4 solutions give the same hyperfine spectra as their negative ions Ar^- do in tetrahydrofuran, although in H_2SO_4 the splitting is larger. The radical forms are believed to be the cations Ar^+, since the distribution of unpaired electrons in the two types are expected to be the same for a given alternant hydrocarbon. It is unlikely that the triplet state would be lowered sufficiently in H_2SO_4 to be responsible for the spectra. Solid complexes with $SbCl_5$ show an exchange-narrowed ESR line, again presumably due to Ar^+ [Weissman, De Boer & Conradi (174)]. The use of an oxidizing medium appears to be necessary for production of the radicals, since they are not found in HF solutions, although the acids are of about the same strength [MacLean & van der Waals (175)].

Mixtures of aromatic hydrocarbons and their anions are ideally suited to a study of the rate of electron exchange between molecules. Over a range of concentrations of $C_{10}H_8$ and its negative ion, the rate constants are in the range 10^7 to 10^9 l./mole sec. No appreciable complex formation between Ar and Ar^- is believed to occur. [Ward & Weissman (176)].

Perinaphthene ($C_{13}H_{10}$) in CCl_4 is presumed to lose one hydrogen to form the symmetrical radical $C_{13}H_9$:
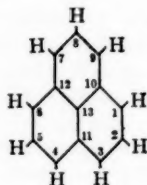
The ESR spectrum consists of seven quartets regularly spaced over an interval of 49 gauss. The unpaired electron density at positions 2,5 and 8 is appreciably smaller than at the other six proton positions, allowing complete resolution and immediate hyperfine assignment [Sogo, Nakazaki & Calvin (177)]. To explain the unusual extent of the spectrum (since the ESR spectra of organic radicals commonly extend over 30 gauss), it is proposed that the spin density is negative at carbon positions 2,3,5, and 10,11 and 12, leading to large positive spin densities at the remaining carbon (and hydrogen) positions [McConnell & Chesnut (164)].

Eleven lines are observed in the hyperfine spectrum of the dibenzene chromium cation $(C_6H_6)_2Cr^+$, although the intensity distribution is that corresponding to thirteen lines. Assuming the latter number to be correct, the twelve proton positions are apparently equivalent. This is expected for chromium centered between the two rings, with strong coupling between the 3-d and the π-electron systems. The g-value is 1.98, appropriate to the presence of three unpaired 3-d electrons [Feltham, Sogo & Calvin (178)]. If one or both of the C_6H_6 rings are replaced by biphenyl, one observes a number of hyperfine components appropriate to a structure with the chromium centered between two rings again. The adjoining C_6H_5 groups make no detectable hyperfine contribution [Elschner & Herzog (179); Razuvaev et al. (180)].

Complexes between electron-donating and electron-accepting molecules, e.g., tetramethyl-p-phenylene-diamine and tetrachloroquinone, may show paramagnetism. Recently four sodium salts of tetrahalogenated quinones have given ESR absorption, demonstrating the great stability of the semi-quinone ions which have been studied extensively in solution [Kainer, Bijl & Rose-Innes (181)]. Further, mixtures of tetrachloroquinone and trialkyl phosphites $(RO)_3P$ have been shown to give colored solutions and strong temporary ESR absorption [Ramirez & Dershowitz (182)].

It had been reported that hexaphenylethane dissolved in such solvents as fluorene or phenanthrene showed no paramagnetism in susceptibility measurements at helium temperatures [Aston, Fritz & Seki (183)]. The failure to detect free radicals was shown to be due to the use of an inductance method for a substance which has $t_1 = 4$ min. at $4.2°K$. One would have had to use a frequency of less than 10^{-3} cps under these conditions, since the susceptibility appears smaller by a factor of $(1/t_1f)^2$ when the frequency f is large compared with $1/t_1$ [Weissman, Feher & Gere (184)].

A new radical with smaller line width appears when tris-p-nitrophenyl-methyl $C(C_6H_4NO_2)_3$ comes into contact with oxygen. Since the second ESR line disappears when the system is evacuated, the new radical is assumed to be the peroxide [Schimmel & Heinecken (185)].

A free radical arising from thianthrene in H_2SO_4 is attributed to an oxidation state intermediate between that of the monosulfoxide and the disulfoxide [Fava, Sogo & Calvin (186)]. If one starts with thiophenol or diphenyldisulfide rather than thianthrene in H_2SO_4, another radical is present. The apparent concentration of both radicals decreases as the temperature is low-

ered [Yokozawa & Miyashita (187)]. At 90°K. solutions of sulfur in oleum show a strong asymmetrical ESR line which is progressively replaced by another on dilution. The latter line is assumed to be due to polymeric sulfur radicals similar to those present in the liquid. Upon raising the temperature, both lines become narrow. The large g-factors of 2.018 and 2.025 are attributed to a spin-orbit contribution of the sulfur [Ingram & Symons (188)].

Phthalocyanines (Co, Cu, Al, and metal-free) as well as a tetraphenyl-porphin appear to undergo a one-electron oxidation. All the intermediates have g nearly equal to 2.002, indicating that the unpaired electron is not associated with a metal atom [George, Ingram & Bennett (189)].

The disappearance of DPPH has long been used as a measure of the number of free radicals of short life. When mixed with benzoyl peroxide or azobutyronitrile, the DPPH ESR signal decays at a measurable rate [Trkal (190)].

Anisotropic contributions to hyperfine splitting are normally not observed in solution because they are averaged out by rapid tumbling. Deliberate increase in the viscosity of a solution showing hyperfine splitting gives rise to broadening because of diminished reorientation rate [MacLean & Baelde (191); van Roggen, van Roggen & Gordy (192)].

ESR absorption in alkali metal-amine solutions has been found to parallel the appearance of an infrared absorption band. The latter is attributed to excitation of solvated electrons (unpaired), while a visible band is assumed to arise from paired electrons [Fowles, McGregor & Symons (193)]. An alternative description as electrons loosely bound to a metal ion in moderately concentrated solutions has been reviewed [McConnell & Holm (194); McConnell (195)].

The most convincing evidence yet adduced for the proposal of Michaelis that oxidation-reduction reactions in biological systems may proceed via one-electron transfers has been obtained in enzyme-substrate systems. ESR absorption has been observed both for oxidation and for reduction of substrates. In intact chloroplasts one obtains on illumination an increased absorption from a radical which exhibits hyperfine splitting [Commoner et al. (196)]. Growth of ESR signals in chloroplasts or dried leaves upon illumination is observed to be as rapid at 135°K. as at room temperature, although the decay is retarded [Calvin & Sogo (197)].

Trapped radicals which are formed by ultraviolet radiation of mixtures of H_2O_2 with alcohols at low temperatures appear to be formed by hydrogen abstraction from alcohol. The symmetrical seven-line spectrum from isopropanol probably is due to the $(CH_3)_2$ COH radical [Gibson et al. (198)]. Other irradiated materials studied include solid nitrogen [Cole et al. (199)] and iodine [Bowers, Kamper & Lustig (200)].

Some new hindered diphenoquinones have been prepared and these show a weak ESR absorption as biradicals [Bourdon & Calvin (201)].

The interesting question of the rate of electron spin exchange in the two halves of a biradical $[(C_6H_5)_2C—C_6H_4—]_2O$ has been investigated by study-

ing the hyperfine splitting due to the ^{13}C nucleus in some of the methyl positions. Taking into account the relative numbers of molecules with ^{13}C—^{13}C, ^{13}C—^{12}C and ^{12}C—^{12}C methyl carbon distributions, three lines with intensity ratios $3:4:3$ were expected for slow spin exchange. These were actually observed rather than five lines with ratios $9:24:44:24:9$. "Slow" exchange here implies a rate small compared with the hyperfine frequency separation of 10^8/sec. [Reitz & Weissman (202)].

Little progress has been made in understanding the nature of free radicals in carbon. One brief note refers to pyrolysis products of silicones [Sugiura & Hatoyama (203)].

Normally one expects dipole-dipole interaction to broaden observed lines. Under unusual conditions of very high magnetization and line width governed by field inhomogeneity, such interaction can lead to a narrowing. When the magnetization $4\pi M$ exceeds the inhomogeneity ΔH, then long-range dipolar forces couple regions in different fields, and these will assume a common resonance frequency. It is impractical to observe this effect in nuclear resonance, though it is shown readily in ferrites. One might hope with a radical like DPPH to see the effect at 20,000 gauss, where the magnetization is about 7 gauss. It is suggested that one should be able to observe the higher modes of magnetic resonance usually seen with ferromagnetics (Geschwind & Clogston (204)].

At present one does not have experimental values for g-factors of individual aromatic radical molecules, since crystal structures are unknown. For a planar molecule with axial symmetry, $g_{||}$ is expected to be close to 2.0023 since only highly energetic transitions can contribute. σ-π transitions tend to increase $g_{\perp}$, being favored by a small separation of these levels and by a large spin-orbit coupling parameter such as one finds for nitrogen or oxygen substitution [McConnell & Robertson (205)].

Line width measurements on stable free radicals include: DPPH [van Gerven, van Itterbeek & de Wolf (206); van Roggen, van Roggen & Gordy (192)].

ESR of defects in solids.—The elegant technique of electron-nuclear double resonance increases experimental resolution by a factor of 10^4 to permit the resolution of individual hyperfine components of an inhomogeneously broadened ESR line. It has been applied to F-centers in KCl, to display a great number of lines arising from ^{39}K, ^{41}K, ^{35}Cl and ^{37}Cl, including quadrupole splittings. The spectra of first shell neighbors as well as that of ^{41}K occur in the sweep range 3.4 to 6.2 Mc. By observing angular dependence, each line can be associated with a particular chlorine lattice site, and inferences made regarding the p-character of the wave function. Extra splittings of some of the lines give a measure of the electric field gradient at nuclei [Feher (207)]. This work has provided an embarrassing fund of information and will constitute a very stringent test of theoretical wave functions. Proper wave functions will lead to appropriate values of g-factors as well as correct isotropic and anisotropic hyperfine structure constants. A

fair amount of progress has been made in such calculations for KCl [Adrian (208)]. The anisotropic contributions to hyperfine interaction are related to the displacement of the g-factor, Δg, from the free electron value. The Δg values allow one to estimate the departure of the unpaired electron wave function from spherical symmetry. Mean values of $(1/r^3)$ have also been calculated for positive and negative ions [Adrian (208)]. Unlike other alkali halides, LiF and NaF without using double resonance display a number of lines separated by the hyperfine constant for alkali ions. The fluorine structure is unresolved [Lord (209)]. Calculations of hyperfine structure have been made for both LiF and NaF [Gourary & Adrian (210)]. Calculations of line width in LiF give a value twice that observed [Kojima (211)]. The second moment of the M-center ESR absorption is estimated as 10,500 gauss² from experiment [Lord (212)]. An attempt has been made to understand this order of magnitude [Gourary & Luke (213)].

The ESR spectra of two new V-centers have been observed in LiF. One center appears to be F_2^- ion associated with a pair of vacancies, while the other seems to be F_3^{-2} with three vacancies (V_4 center). An assignment of the geometry of the mixed s-p wave functions and of s- and p-components has been made [Cohen, Känzig & Woodruff (214)].

The F-center spectrum in MgO gives an unusually direct verification of the model of a trapped electron at a negative ion vacancy. Those electrons surrounded only by ^{24}Mg or ^{26}Mg $(I=0)$ give a single intense ESR line. Electrons with one or two ^{25}Mg neighbors $(I=5/2)$ give respectively six- and eleven-line spectra when the field is along the [111]-direction. The central line is isotropic, having been observed in powders. The trapped electron is localized to a greater degree than in the alkali halides. [Wertz et al. (215)].

Paramagnetic ions in crystals.—Evidence for the existence of positive ion vacancies associated with Cr^{+3} in the nearest or next-nearest neighbor positions is inferred from the appearance of spectra of respectively rhombic and of axial symmetry. The next-nearest position is favored, unlike the case of Mn^{+2} in quenched NaCl. The alternative explanation of a unipositive ion in place of a vacancy cannot be accepted because of the low concentrations present [Wertz & Auzins (216)]. Since one positive ion vacancy compensates the extra charge of two trivalent ions, one finds also numerous Cr^{+3} ions in a field of strictly cubic symmetry. It is likely that uniform shrinkage of the oxygen octahedron occurs about the chromium ion [Low (217); Wertz & Auzins (216)]. Chromium has also been observed in Al_2O_3, where the $1/2 \leftrightarrow -1/2$ transition gives a line which is narrower than the remaining two, owing to interaction with the aluminum [Manenkov & Prokhorov (218)]. Cr^{+3} was incorporated into a crystal of ferroelectric guanidinium aluminum sulfate hexahydrate to look for effects of the polarization field, but none were observed [Bogle, Gabriel & Bottomley (219)].

Manganese in AgCl or AgBr shows hyperfine structure at low concentrations without indication of vacancy association. At higher concentrations in AgCl only a single line is observed [Abe (220)].

Eu^{+2} and Gd^{+3} are found naturally occurring in CaF_2, both giving splittings appropriate to a cubic crystalline field [Ryter (221)]. The cubic field splitting pattern of these ions has been calculated [Lacroix (222)].

Multiple ESR absorption lines in silicate glasses and in fused silica appear to be correlated with optical absorption bands [van Wieringen & Kats (223)].

Some evidence for the formation of Fe^+ and Cr^+ in electron or γ-irradiated NaF is obtained by analogy with the behavior of the isoelectronic ions Co^{+2} and Mn^{+2}. The lines have isotropic g-values of 4.28 and 1.998 respectively [Bleaney & Hayes (224)]. Lines after irradiation have also been observed for what appear to be Co^+ and Ni^+ but not for Mn^+, although the Mn^{+2} spectrum disappears [Hayes & Jones (225)].

An ESR study of hemoglobin reveals that $g = 2$ for heme groups with the magnetic field lying in their plane, and $g = 6$ when the field is at right angles. Contrary to previous assumptions, the heme groups do not all lie in a plane [Bennett, Gibson & Ingram (226)].

The observation of seven fine-structure lines due to curium in $LaCl_3$ is interpreted as evidence for seven 5f electrons [Fields et al. (227)].

Under increasing hydrostatic pressure, $NiSiF_6 \cdot 6H_2O$ shows a decrease in axial fine structure splitting constant to zero, at which point the line width is a minimum. Further increase in pressure leads to crossing of lines. The crystal field changes probably occur because of anisotropy of compressibility. It would appear that much detailed information is potentially available with this procedure [Walsh & Bloembergen (228)].

To account for the large hyperfine splitting of Mn^{+2}, it is suggested that the exchange interaction between 3-d and 2-s or 3-s electrons depends upon whether the d-electron spins are parallel or antiparallel to those of the s-electrons. This would lead to incomplete pairing of the latter and hence a strong hyperfine interaction [Heine (229)].

In a study of the angular dependence of absorption in $CuSO_4 \cdot 5H_2O$, the absorption tensor is found to be uniaxial [Sundaramma (230)].

The Hamiltonian for the plutonyl ion has been solved and the g-components calculated [Eisenstein & Pryce (231)].

Term splittings are given for the thirty-two crystal classes [Fick (232)].

The ground state of $^{233}UCl_3$ in $LaCl_3$ is found to have $S = 1/2$, $I = 5/2$. Multiple-quantum transitions are observed [Dorain, Hutchison & Wong (233)]. The zero-field splitting of Gd^{+3} in $LaCl_3$ is small, but its temperature dependence is appreciable. Various S-state splitting mechanisms are examined [Hutchison, Judd & Pope (234)]. Splitting mechanisms for Mn^{+2} and Fe^{+3} include internal spin-spin interaction [Watanabe (235)]. Ammonium chrome alum has been reinvestigated [Davis & Strandberg (236)]. Pr^{+3} studies were made by Gränicher, Hübner & Müller (237). Icosahedral fields study was made by Judd (238).

A series of papers by Orgel has caused inorganic chemists to start thinking about complex formation in transition group elements in terms of crystal field theory [Orgel (239)]. In solution one may postulate the formation of

microcrystals from solvent molecules or complexing groups, the unit having a spin Hamiltonian similar to that for an ion in a crystal. The observed line width depends upon the resultant electric field symmetry. Factors which in a crystal give rise to anisotropy produce line broadening in solution. Proximity of the first Stark excited state to the ground state gives a similar effect. [McGarvey (240)].

Nuclear resonance in paramagnetics and antiferromagnetics.—In all of the following compounds, CoF_2, FeF_2, FeF_3, NiF_2, and CuF_2, the fluorine resonance is shifted to lower fields, while in CrF_3 no shift occurs. These large shifts (1.2 per cent in FeF_3) and their angular dependence are presumed to arise by partial electron transfer from fluorine to the metal ion. The resulting fluorine polarization is proportional to the spin polarization of the metal ion [Jaccarino, Shulman & Stout (241)]. In CrF_3 all electrons are in d-ϵ orbitals, and one expects no σ- bonding or marked resonance shift [Baker & Hayes (242); Jaccarino, Shulman & Stout (241)]. A partial electron transfer from copper to chlorine is likewise presumed to occur in the antiferromagnetic state of $CuCl_2 \cdot 2H_2O$ [Rundle (243)]. That such large displacements of nuclear resonance can also occur for next-nearest neighbor nuclei has been shown in $LiMnO_4$. Both ^7Li and ^{31}P show a shift, the electron deficiency at the latter being nearly the same as for fluorine in MnF_2 [Mays (244)]. The previous failure to observe the fluorine resonance in the antiferromagnetic state of MnF_2 has been shown to be due to the displacement $\Delta\nu$ of resonance frequency to values far above those ordinarily used. The applied fields are very small compared to the internal fields at F nuclei. Observations were made in the range 152 to 168 Mc. at fields of 300 to 3000 gauss. Since one has two separate oppositely aligned lattices, the resonant absorption is expected at $\Delta\nu \pm \gamma H_0/2\pi$. Both lines have been observed [Jaccarino & Shulman (245)].

Observations at low fields.—The polarization M_z of DPPH subjected to an intense r-f field modulated at a low frequency is monitored by a pickup coil parallel to the applied field H_z. Using circularly-polarized r-f field H_1, modulated by a 280-cycle square wave, the behavior was that predicted by the Bloch equations modified to include relaxation toward the instantaneous applied field. A net polarization M_x remains when $H_x = 0$, as predicted. A peak observed at negative field values is ascribed to a small counter-rotating component (Bloch-Siegert effect) [Whitfield & Redfield (246)].

Observations on $Na - NH_3$ solutions at low frequencies (60–250 Kc.) with crossed coils gives mixtures of absorption and dispersion. The two susceptibility components are given as a function of applied field [Beeler & Roux (247)].

Proton resonance has been observed in water at fields as low as 0.7 gauss without the aid of artificial polarization [Rocard (248); Rocard, Béné & Extermann (249)].

Optical pumping.—An extensive investigation of the Stark effect in optical-magnetic resonance of mercury atoms includes line-shape studies for

three unequally spaced levels [Blamont (250)]. Other studies have been made using electron bombardment to produce polarized emission and therefore the unequal population of magnetic levels which is required for detection of magnetic resonance transitions [Pebay-Peyroula, Broussel & Kastler (251, 252); Lamb (253)].

In an attempt to determine how long an ESR relaxation time may be attained, sodium vapor was diluted with argon. The maximum t_1 found was 0.21 sec., [Dehmelt (254)]. It has been found possible in optical pumping experiments to obtain modulation of the pumping radiation at the precession frequency [Dehmelt (255)].

Miscellaneous studies.—Other studies include calculation of sixth moments [Glebashev (256)]; observations of rotation of the plane of polarization when H_z and H_1 are at right angles [Hedvig (257)]; possibility of observing nuclear resonance in salts of Eu^{+3} [Elliott (258)].

Apparatus and techniques.—Probably the most generally useful paper of 1957 on ESR techniques is one which treats most of the practical aspects of spectrometer design and use [Feher (259)]. It is made clear that "optimum" arrangements are modified by particular requirements.

An indirect evaluation of the second moment of the absorption line is based on the expansion of a modified Kramers-Kronig relation in an inverse power series of the frequency deviation from the line center. The coefficients in the expansion are related to the zeroth, first, second, etc., moments. By fitting the wings of a dispersion curve with such a series, the second moment is obtained. In a modification of this approach, one may expand the n'th moment of a line as a series of integrals. If with sinusoidal sweep one had alternate signals opposite in phase, the terms in this series would constitute the Fourier components of the signal. Such inversion was accomplished and a harmonic analyzer used to measure frequency components. For a carbon free radical a satisfactory value of the second moment was obtained. However, for an exchange-narrowed free radical, the true extent of the line is so great that the sweep was insufficient to encompass the line completely [Hervé (260)].

A distinction between quadrupolar and magnetic relaxation mechanisms in a solid with a nucleus spin 3/2 may be made by comparison of the saturation curves of the central and outer line components. These differ appreciably if the mechanism is quadrupolar [Andrew & Swanson (261)].

Normally the undesired rotating component of a linearly-polarized r-f field does not produce detectable effects. However in double resonance experiments in which one saturates one set of nuclei at a frequency close to that of a second set, the latter resonance frequency may be observably displaced Lösche (262).

The design of a simple spin echo unit operating at audio frequencies in the earth's magnetic field is a commendable achievement. This inexpensive equipment should permit many more laboratories to make useful relaxation time measurements [Powles & Cutler (263)].

It is shown that by using proper precautions, one may apply the Carr-

Purcell technique of a series of pulses to measure very long t_2 values [Pfeifer, Winkler & Ebert (264)].

Free nuclear precession may be observed with good sensitivity with a bridge arrangement if the receiver used as a detector is slightly detuned [Benoit & Klein (265)].

Other papers on equipment or techniques are as follows: Production of homogeneous magnetic fields [Primas & Günthard (266)]; magnet current stabilizer [Abraham, Ovenall & Whiffen (267)]; field stabilizer [Primas & Günthard (268)]; nuclear resonance spectrometers [Mitchell & Eisner (269); Baker & Burd (270); Primas (271); ESR spectrometers [Feher (3); Bowers, Kamper & Knight (272); Llwellyn (273); Borel & Manus (274); Rose-Innes (275); Uebersfeld & Erb (276); Ryter (277)], temperature control units [Shoolery & Roberts (278); Mulay (279)]; standardization procedures and shielding measurements [Zimmerman & Foster (280)]; oscillating detectors (Shpiegel, Raiser & Miae (281)]; bridge balance [Collins (282)]; intensity measurement (Greim & Richter (283)]; modulation corrections [Spry (284)]; spin echo equipment [Schwartz (285)]; use of self-inductance of capacitor [Gersh & Lösche (286)]; double modulation to achieve apparent line narrowing [Unterberger, Garcia de Quevedo & Stoddard (287)]; use of "ringing" after line passage to determine t_2 [Pomerantsev (288)].

Nuclear moment and spin determinations.—Magnetic moments which follow are given in nuclear magnetons: ^{3}He, sign negative [Klein & Holder (289)]; ^{21}Ne, -0.661758 [LaTourette, Quinn & Ramsey (290); ^{58}Co, ±4.052 [Dobrov & Jeffries (291)]; ^{81}Rb, $+2.05$, ^{82}Rb, $+1.50$, ^{83}Rb, $+1.42$, ^{84}Rb, -1.32 [Hubbs *et al.* (292)]; ^{91}Zr, -1.29802 [Brun, Oeser & Staub (293)]. Magnetogyric ratio of the proton: 26755.6 gauss^{-1} sec.$^{-1}$ [Wilhelmy (294)]. Magnetic moment ratios are: ^{115}In/^{113}In, 1.0021437 [Rice & Pound (295)]; ^{151}Eu/^{153}Eu, 2.264 (2.24) [Abraham, Kedzie & Jeffries (296); Manenkov *et al.* (297)]; ^{152}Eu/^{151}Eu, 0.5574, ^{154}Eu/^{153}Eu, 1.308 [Abraham, Kedzie & Jeffries (296)]; ^{207}Pb/^{1}H, 0.2092198 [Baker (105)]; ^{235}U/^{233}U, -0.65 [Blaise, Gerstenkorn & Louvegnies (298); Dorain, Hutchison & Wong (233)].

Spin determinations are as follows: ^{32}P, $I=1$ [Feher, Fuller & Gere (299)]; ^{57}Fe, $I=1/2$ [Garif'yanov, Zaripov & Kozyrev (302); Wertz & Auzins (303)]; ^{76}As, $I=2$ [Pipkin & Culvahouse (145)]; ^{91}Zr, $I=5/2$ [Brun, Oeser & Staub (293)]; ^{141}Ce, $I=7/2$ [Kedzie, Abraham & Jeffries (300)]; ^{147}Nd, $I=5/2$ [Kedzie, Abraham & Jeffries (300)]; ^{152,154}Eu, $I=3$ [Abraham, Kedzie & Jeffries (296)]; ^{233}U, $I=5/2$ [Dorain, Hutchinson & Wong (233)]; ^{235}U, $I=7/2$ [Blaise, Gerstenkorn & Louvegnies (298)]; ^{239}Np, $I=1/2$ [Abraham *et al.* (301)].

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RADIATION CHEMISTRY[1]

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Several congresses and discussions on radiation chemistry or related subjects were held during the past year. The Radiation Research Society's fifth meeting was held in New York on May 13 to 15, 1957, and the first colloquium on radiation chemistry in Moscow, March 27 to April 2, 1957. A number of papers dealing with radiation damage, dosimetry and radiation induced polymerization, were presented at the UNESCO International Conference on Radioisotopes in Scientific Research in Paris, September 9 to 21. An informal meeting on radiation produced organic peroxides and radiobiology was held at the Institut du Radium, Paris.

Garrison (1) published a review on radiation chemical research reported during 1956, and Pchejetzky & Dmitriev (2), a critical paper dealing with mechanisms of radiation induced chemical reactions. A series of reviews on different aspects of radiation chemistry appeared in Japan (3).

GASES

A considerable effort has been made in the past few years toward the determination of W, the energy required to produce one ion pair for a number of gases and mainly for air. There were discrepancies between early work, which has been summarized by Gray (4), and recent data. An accurate knowledge of W is necessary for dosimetry measurements, calibration of ionization chambers, and also for the understanding of the ionization process itself. The present situation regarding the absolute value of W for different gases has been summarized by Weiss & Bernstein (5). With the exception of helium gas the results from alpha particles are in close agreement whether obtained from polonium (6a) or plutonium (7). The value of 35 ev for W in air may now be given with a probable experimental error of 1 per cent, as may the values 26.5 ev for argon, 36.5 ev for hydrogen, 36.5 ev for nitrogen, 32.5 ev for O_2, and 34.4 ev for CO_2. There is still a discrepency for helium and the theoretical value (43.5 ev) from Miller (8), lies between the two experimental values of 42.7 ev and 46.0 ev.

In the case of electrons the most recent results of Jesse & Sadauskis (6a) and Weiss & Bernstein (9) are in close agreement within the probable error of ± 1 per cent. For β particles from S^{35}, which has a distribution curve of known shape, the energy W has been determined with 4π counting, in nitrogen, ethylene, and ethane (6b). Respective values of 35.3, 26.2, and

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[1] The survey of literature pertaining to this review was concluded November, 1957.

[2] The author is indebted to Dr. A. M. Peers for grammatical corrections in the text.

24.7 ev were found in agreement with W for α-rays. For air the average value of 34.0 ev ± 0.6 is claimed to represent the best value available at present and seems definitively higher than the earlier figure of 32.5 ev.

Electron impacts.—Electron impact studies were carried out during 1957 mainly on ethyl halide (10) and benzene derivatives (11). The technique of using mass spectrometry for determination of the nature and the ionization potential of organic ions in the gas phase, and for the knowledge of different bond energies is of great interest for the radiation chemistry of organic compounds. Irsa (10) has shown that the main ions formed by electron impact on ethyl halides were $C_2H_5X^+$, $C_2H_5^+$, and also CH_2X^+. The last ion would be produced simultaneously with a CH_3 radical. Only for ethyl iodide, a subsidiary reaction gives the ion HI^+ ($C_2H_5I + e = HI^+ + CH_2 = CH_2 + 2e$). Interesting data were calculated for the ionization potentials of C_2H_5Cl, C_2H_5Br, and C_2H_5I, for which the higher possible values are respectively 11.2, 10.7, and 9.6 v. Upper limits for bond energies of C—Cl, C—Br and C—I were found to be 3.6, 2.8, and 2.4 v, respectively.

The well-known stability of the benzene ring to chemical and radiation attack has led to the assumption that the ions found in the mass spectra of alkyl benzenes, heavier than toluene, are phenyl ions ($C_6H_5^+$) formed by cleavage of the side chain from the ring. Meyerson & Rylander's (11) research with labeled molecules furnishes evidence that $C_6H_5^+$ ions derived from phenyl alkyl ketones and from 2-methyl-2-phenyl-alkanes apparently retain the original ring intact, although some $C_6H_6^+$ is formed as a minor product from acetophenone dissociation. But, on the other hand, the spectra of labeled α-chloroethylbenzene and ethylbenzenes show a process which involves ring cleavage. There is no simple rupture of the bond between ring and substituent. Furthermore, the intensities of the $C_6H_5^+$ ions from deuterated ethylbenzene and unlabeled ethylbenzene are by no means what they should be if the $C_6H_5^+$ ion were formed by cleavage of the side chain from the ring.

Melton & Rosenstock (12) have studied collision induced dissociations in the mass spectrum of methane. A number of diffuse peaks at nonintegral masses was found to arise from dissociation of methane fragments on collision with residual methane gas. Single collision processes produce CH_3^+, CH_2^+, and other ions. The comparison with the mass spectrum formed by electron impact is striking, both for the nature of the ions and their relative abundance. The same sort of work was also carried out with n-butane and i-butane. In a similar way, positive ion-molecule collisions and negative ion-molecule collisions were investigated in formic acid with the mass spectrometer (13). Both positive and negative ion fragments can be produced with rather large cross-sections.

The bond energy of nitrogen has been found to be $D(N_2) = 9.76$ ev by reflected shock velocities measurements (14); the value is in close agreement with that determined by electron impact.

Experiments on electron capture, electron loss, and ionization were

pursued by De Heer *et al.* (15) with mass spectrometers on mixtures of nitrogen, argon, krypton, and hydrogen ions in hydrogen, and helium ions in argon.

The degradation of the energy released by α particles in noble gases was considered by Platzmann (16). For helium, 20 per cent of the energy is expended in raising the atoms to higher excited levels.

The luminescence induced by α-rays in argon, carbon dioxide, and nitrogen, together with mixtures of these gases with quenching vapors was studied with a photomultiplier tube by Brown & Miller (17). The emission by CO_2 rose rapidly as the pressure was increased and reached a value independent of pressure over a wide range, in agreement with the application of the Stern-Volmer relation to $CO_2 \leadsto CO^*$ ($^1\Sigma^+$). The CO^* ($^1\Sigma^+$) is quenchable by CO_2 and by hydrogen. The contamination and excitation transfer to mercury vapour was also observed. Results on argon and nitrogen show spectra of luminescence similar to those of the luminescence brought about by the electric discharge. Energy transfer by collision was observed. In the best conditions the yields of visible and near ultraviolet light were not larger than 0.5 quanta per 100 ev.

Gas radiolysis.—For inorganic gases early studies using radon or polonium α-rays are now replaced with either pile radiation or with cyclotron beams. An interesting and novel technique of irradiation was developed which used direct impact of the fission fragments of uranium-235 on the gases (18a). The dosimetry calculations seem to be laborious, but the authors used nitrous oxide as a gas chemical dosimeter which was previously calibrated [Harteck & Dondes (18b)]. With five mg. of uranium-235 oxide powder and a flux of $3 \cdot 10^{12}$ neutrons/cm^2/sec (in the Brookhaven reactor), the nitrous oxide decomposition was increased by a factor of 60 to 200 depending on conditions, and the ratio of the decomposition products was the same as with pile radiation. The decomposition of nitric oxide and nitrogen dioxide under these conditions was carefully studied (18c). It seems that NO^* molecules, excited by the impact of fission products, dissociate into N and O. The decomposition follows through the main reactions $NO + N \rightarrow N_2 + O$ and $2NO + O_2 \rightarrow 2NO_2$, in such a way that for one primary excited NO^* three additional NO molecules are destroyed. Therefore, the initial yield of the radiolysis, which is equal to 13.8, corresponds to a primary yield of 3.45 ± 0.35 NO molecules per 100 ev. When NO is consumed, the yield of NO_2 decreases very sharply because of the reactions $NO_2 + N \rightarrow N_2O + O$ and $NO_2 + N \rightarrow 2NO$, and a steady state is reached for O_2, NO_2, N_2O and N_2. The radiolysis of nitric oxide has also been studied. It yields N_2, N_2O and O_2 and is autocatalyzed by N_2 and N_2O.

The decomposition of N_2O which was previously studied under ionizing radiations has also been investigated by Zelikoff & Aschenbrandt (19) who irradiated the gas by krypton resonance radiation in the far ultraviolet at 1236 A. The decomposition products, N and NO, and the mechanisms are the same as for the pile radiation decomposition.

The decomposition of carbon dioxide by pile radiation and fission product impact has also been investigated by Harteck & Dondes (18a). The work is an extension of previous research (20) in which the same authors had shown that the very small yield of the radiolysis was due to recombination reactions like $CO+O+M \rightarrow CO_2+M$, and the presence of very small quantities of NO_2 inhibits the back reaction. The carbon dioxide radiolysis G value at a pressure of one atmosphere is equal to 0.005 and the addition of 1 per cent of NO_2 increases the yield to 8.5 ± 0.5. For higher pressures, G reaches 0.5 without inhibitor but stays at 8.5 when inhibitors are present. On the other hand, liquid CO_2 was decomposed with a G value of 4 to 5 whether or not inhibitors were present.

Pure water vapor was irradiated with tritium β-rays by Firestone (21), who confirmed early results from Duane & Scheuer (22), on the very low yield of decomposition (upper limit for $G(H_2) = 0.02$) because of back reactions. On the other hand, Firestone found that in mixtures of tritium-water vapor and deuterium gas at mole fractions in the range 10^{-3} to 10^{-2}, the rate of hydrogen deuteride formation was $G = 11.7$ for nonchain temperature independent exchange. This value indicated a radical-pair yield which was about three times greater in water vapor than in liquid water. It seems, as expected, that a much greater proportion of radicals are free to react with solute molecules in the gas phase.

Ion-molecule reactions.—Research on the mechanism of gas radiolysis has been reoriented since Stevenson & Schissler (23) concluded from their experimental work on mass spectrometry that ion-molecule reactions occur for each collision, and that their cross section is three times larger than the cross section for neutral particles calculated by kinetics theory. In the same laboratory where Essex *et al.* have worked on the influence of electric fields on the radiolysis of ammonia and N_2O, Burtt & Zahlan (24) have shown that the yield of decomposition of ammonia by α-rays increases when the pressure is decreased, a result which is in agreement with a radical mechanism of the same type as the scheme proposed by McDonald *et al.* (25), for the photochemical decomposition, through NH_2, N_2H_4, N_2H_3, and N_2H_2 radical reactions. On the other hand, the intensity effect which was not found in the photochemical work is attributed by the authors to ion-molecule reactions such as $NH_3^+ + NH_3 \rightarrow NH_2 + NH_4^+$ and others. NH_4^+ is neutralized at the wall which becomes rich in NH_3 and atomic hydrogen. The pressure controls the diffusion of radicals to the wall and the intensity determines the relative importance of the gas phase and the wall reactions. If the pressure is not too high and if the intensity decreases, NH_2 radicals will not all react homogeneously in the gas phase, but wall reactions become more and more important. When NH_2 diffuses to the wall it combines with H atoms, generates NH_3, and therefore lowers the decomposition yield.

Recent work on irradiation of methane by high energy electrons seems also to prove that it is difficult to admit a completely free radical nature for the reaction (26). The results are essentially the same as early results ob-

tained with α-rays by Lind & Bardwell (27). The decomposition yield and the hydrogen yield are in both cases $G = -7.6$ and $G_{H_2} = 5.5$. C_2H_6, C_3H_8, C_2H_4, and C_4H_{10} are formed at much smaller rates. These are independent of pressure and seem to be also independent of intensity over a wide range. It is therefore difficult to reconcile these facts with the purely free radical scheme which would be required if CH_4^+ and CH_3^+ were neutralized before reacting with methane. Also the ethane formation cannot be explained completely on the basis of radical-radical combination. If C_2H_5 radicals were formed by neutral combination: $CH_3 + CH_2 = C_2H_5$, there would be found in mass spectrometry a disappearance of C_2H_5 in irradiated methane when the radicals are "scavenged" by iodine. The experiment was made by Gevantman & Williams (28) who did not find any change in relative concentrations of CH_3, CH_2, and C_2H_5 when the concentration of added iodine was varied. These facts suggest that ion-molecule reactions in irradiated methane may be playing a much larger part than has been generally believed, such as $CH_4^+ + CH_4 = CH_5^+ + CH_3$ and $CH_3^+ + CH_4 = C_2H_5^+ + H_2$.

Lampe has carried out another interesting study of high energy electron irradiation of neopentane (29) where the numerous gaseous products were analyzed by partition gas chromatography. The most important reaction which follows the ionization of neopentane seems to be $C(CH_3)_4^+ \rightarrow C(CH_3)_3^+ + CH_3$. Therefore, CH_4 and C_2H_6 are probably formed by the usual reactions of abstraction and combination from CH_3 radicals.

Dewhurst & Winslow (30) have made a comparison of the radiolysis of n-hexane by radiocobalt γ-rays and by electrons produced at 800 kv. The products which were analyzed by gas chromatography are the same with the two kinds of radiation, as was expected, since the mean energy of the electrons is not very different. However, the yields are different mainly for the products in C_8 to C_{10}. The authors suggest that with very high dose rates delivered by electrons ($4 \cdot 10^9$ higher than with γ-rays) the absorption of the energy is much more homogeneous and the interactions between ion "spurs" increase the yield of products in C_8 to C_{10}. We shall find a similar phenomenon for irradiation of aqueous solutions at high dose rates.

Retardation effect.—In their early work Lind & Bardwell (31) found that the reactions induced by α-rays on a number of gases were enhanced by foreign gases. This was interpreted as transfer of ionization from foreign gas to the reactant because of the relative ionization potentials. In a recent publication Lind & Rudolph (32) report a case where, on the contrary, the addition of a foreign gas causes retardation; namely acetylene polymerization by α-rays (ionization potential of 11.43 v) is retarded by benzene (9.25 v), in a similar manner to the protective action of benzene in the liquid phase polymerization of cyclohexane (33).

Radiolysis of ethylene and of several other gaseous hydrocarbons by electrons was also studied by Mikailov *et al.* (34).

Before finishing with gas reactions, it seems useful to emphasize the importance of novel techniques which are able to permit a new development

of radiation chemistry in the gas phase. We have already quoted the fission product impact as a valuable source of radiation. Gas chromatography analysis is going to give much information for organic products. The use of alphatron gauges provides facilities for gas analysis of inorganic gases.

ORGANIC COMPOUNDS IN LIQUID PHASE

Two different approaches to the radiation chemistry of liquid organic compounds can be defined for the past year. On one hand, some progress was made in the knowledge of basic mechanisms of ion and radical formation and distribution, mainly by studies with radioiodine scavengers and with labeled molecules. On the other hand, more practical preoccupations were the use of radiation energy for making new organic materials and helping addition reactions and synthesis, and measurement of the radiation resistance of organic substances which might be useful in nuclear reactors, as moderators, coolants or as reagents for chemical radioactive processes.

Basic mechanism of radiation reactions.—A new approach to the study of processes involved in the radiolysis of organic compounds has been proposed by Schulte (35). By introducing a solute at a low concentration (a technique analogous to that already in use for aqueous solutions) the author was able to show evidence for the nonhomogeneous mode of action of γ-radiations on carbon tetrachloride. Labeled chlorine was added as a solute to CCl_4 and the rate of the radiation induced exchange of chlorine with CCl_4 was measured. It was shown that two main reactions occur, the yield of which is independent of chlorine concentration within $7 \cdot 10^{-4}$ M and $7 \cdot 10^{-3}$ M. The first is the radiation induced exchange

$$1/4 \; CCl_4 + 1/2 Cl_2{}^* \rightsquigarrow 1/4 \; CCl_4{}^* + 1/2 \; Cl_2$$
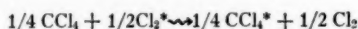
The measurement of its rate gives the yield for radicals which escape local combination. The main radical is assumed to be CCl_3 which exchanges with Cl_2 thusly:

$$CCl_3 + Cl_2{}^* \rightarrow CCl_3Cl^* + Cl,$$
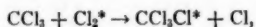
at a yield of $G(CCl_3) \leq 3.5 \pm 0.35$. A second reaction happens in *spurs* (particle tracks) and yields C_2Cl_6 by combination of CCl_3 radicals. Its G value would be 0.8 ± 0.06. This interpretation is very similar to the mechanism of water radiolysis. Differences between the rates of diffusion of Cl atoms and CCl_3 radicals from the *spurs* lead to different yields for the combination of Cl atoms into Cl_2 and the combination of CCl_3 into C_2Cl_6.

The radioiodine scavenging method has now been extensively used for several years. Recently McCauley & Schuler (36) have applied it to the study of radical production in the radiolysis of liquid butane. The scavenging seems at first not to be efficient since the measurement of the yield of all the alkyliodides produced indicates an increase from $G = 5.6$ to $G = 9.0$ when the iodine concentration was increased from $2 \cdot 10^{-3}$ M to $2 \cdot 10^{-2}$ M. But for each individual iodide, the yield is constant, the increase being due to for-

mation of high boiling point di-iodides when the concentration was increased. The most interesting conclusion drawn from their work is that we must also admit ionic reactions for liquid phase radiolysis. The experiment showed that the proportion of n-propyl radicals over methyl radicals was about one-fourth although purely radical reactions should give as much CH_3 as n-C_3H_7. Therefore, the authors think that homolytic reactions of ionic nature occur on butane molecules. Strong evidence for ion-molecule reactions were also found for methyl iodide radiolysis in the liquid phase. Schuler (37) concludes that CH_3^+ reacts with CH_3I to give $C_2H_6^+ + I$ and also $CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$.

A slightly different study using addition of iodine was carried out by Burton et al. (38). It shows that iodine is not only a scavenger but also can prevent chemical reactions by interfering in the decomposition process of the excited species present. When cyclohexane is irradiated in presence of iodine, the G value of hydrogen yield is lowered from 5.9 in pure cyclohexane to 3.8 for the mixture. On the other hand it is well known that benzene lowers the hydrogen yield when added to cyclohexane. According to the early suggestion of Manion & Burton (33), benzene receives excitation energy from singlet-excited cyclohexane but does not itself decompose. Therefore, addition of benzene to a mixture of cyclohexane and iodine results, as was expected, in a further decrease of $G(H_2)$ when the benzene concentration is large enough. However, for low benzene concentrations, a maximum of $G(H_2) = 4.0$ is observed. Experiments with benzene-d_6 proved also that $G(H_2)$ comes entirely from the C_6H_{12}. According to the authors, two principal mechanisms occur for H_2 production from pure cyclohexane, depending on the excited state which is reached. When C_6H_{12} is excited at a singlet state, then the reaction is $C_6H_{12}^* \rightarrow C_6H_{11} + H$. But if it is in a triplet state $C_6H_{12}^* \rightarrow C_6H_{10} + H_2$ occurs. Iodine in pure cyclohexane would induce an internal conversion from triplet state to ground state and therefore suppress the second reaction. Benzene at low concentration induces one or several reactions by which the singlet state is produced for cyclohexane instead of the triplet state. Therefore, in a mixture of C_6H_{12}, I_2, and benzene, where triplet states are chemically unproductive, the magnitude of $G(H_2)$ and $G(-I_2)$ are increased. When the benzene concentration becomes higher, the first reaction is also suppressed and the yield decreases.

Experiments on radiolysis of methanol in the absence and presence of iodine have been performed and indicate also that iodine not only scavenges H atoms and other radicals but also induces conversion to the ground state (39).

Bouby & Chapiro (40) measured the radical yield with diphenylpicryl-hydrazide in a mixture of methyl acetate and benzene. From experiments with low benzene concentrations it appears that the energy transfer is enhanced when the mixture is irradiated in presence of air and that the protective effect of benzene is much larger than in vacuo.

The mechanism of radiation-induced decomposition of ethanol has

been investigated by Burr (41) with deuterated molecules. The results provide a very convincing proof of the formation of the $CH_3\dot{C}HOH$ radical and hydrogen evolution. Percentages of deuterium in the H_2 evolution during the radiolysis of CH_3CH_2OH, CD_3CH_2OH, CH_3CD_2OH, CH_3CH_2OD, and CD_3CD_2OD show very clearly that the formation of acetaldehyde and 2,3-dihydroxybutane must be attributed to attack on the ethanol molecule at the —CH_2— position, as it has been suggested by McDonell & Newton (42). Mass spectrometry experiments were performed at the same time, and they showed that H loss was large for CH_3CH_2OH and CD_3CH_2OH and small for CH_3CD_2OH. On the contrary, D loss was large for CH_3CD_2OH although the isotopic effect should have led to the opposite result if there was no preferential attack.

Since the first work on ethyl iodide in 1948, by Lefort *et al.* (43), more than ten papers have appeared on the radiolysis of alkyl iodides, but the mechanisms are not completely elucidated. Previous experiments (44) on liquid ethyl iodide, *n*-propyliodide and isopropyliodide seemed to have proved that the iodine produced by the initial reaction was sufficient to scavenge all the homogeneously distributed radicals (thermal radicals), via the reaction $R+I_2=RI+I$, and that the observed products were formed only by hot reactions in radiation tracks, where the concentration of free radicals was high. However, the experiments of Willard and his co-workers (45, 46) establish the fact that organic thermal radicals, produced during the radiolysis of degassed ethyl iodide, do not all react with I_2. The mechanism of radiolysis includes not only the production of HI, I_2, alkyl radicals, and hydrocarbons within the radiation tracks, but also reactions of the thermalized radicals outside the tracks with HI and I_2. This interpretation is supported by the decrease in iodine yield, $G(I_2)$, caused by added iodine, the increase in $G(I_2)$ caused by added hydrogen iodide, and the increase in exchange yield between radioiodine and ethyliodide caused by added iodine. A quantitative treatment of the results gives the rate of elementary reactions on the basis of a reaction scheme in two parts: (*a*) in radiation tracks $C_2H_5I \rightsquigarrow C_2H_5I^*$ $\rightarrow C_2H_4+HI$, and also $C_2H_5I^* \rightarrow C_2H_5+I$, $C_2H_5I+C_2H_5 \rightarrow C_2H_4+C_2H_6+I$; (*b*) for thermal radicals, $C_2H_5+I_2 \rightarrow C_2H_5I+I$, $C_2H_5+HI \rightarrow C_2H_6+I$. The rate of iodine production and of exchange of radioiodine are also dependent on the ratio of oxygen concentration to iodine as well as on the ratio of iodine concentration to HI (45). This indicates again that the yields, both in the presence and absence of oxygen, are determined by competitive reactions which consume thermal radicals. Experiments were made with a number of alkyl iodides; they confirm the results of Hamill and co-workers (47) concerning the dependence of $G(I_2)$ on the β-hydrogen content of the alkyliodides. All the iodides show a linear increase in iodine production with increasing energy absorption up to about a concentration of iodine of $10^{-3}M$. However, there is a curvature toward lower G values for higher concentration of iodine. This deviation may be due to a reaction between HI and some reaction product which decreases the rate of HI accumulation and of $R+HI$

→RH+I. $G(I_2)$ was found to be independent of temperature in the liquid phase but to have a positive temperature coefficient in the crystalline solid phase. The orientation of the molecules with respect to each other seems to be an important factor in determining the chemical consequences of the energy absorption because it has been observed that the yields were higher in the glassy state than in the crystalline state at the same temperature ($-190°$) for both CH_3I and C_2H_5I.

Radiation resistance.—The decomposition of terphenyls under radiation has been studied by Colichman & Fish (48). There is a small polymerisation into hexaphenyl, paraterphenyl being more stable than ortho and meta. Copper phthalocyanine was found to be very stable under radiation (49). Goode (50) has shown that tributyl phosphate extraction was affected both because of radiation-induced oxidation of diluant naphtha and radiolysis of tributyl phosphate which is quite sensitive. For example, the decontamination factor for uranium decreases from 5000 to 21 when the exposure to pile radiation is increased from 0 to 280 watt-hr/liter.

Aqueous solutions of 8-hydroxyquinoline, which are very useful for analytical reactions, are very stable to radiation and may be employed for activities of the order of several curies. The radiolytic products were isolated by paper chromatography [Kertès *et al.* (51)].

Radiation induced reactions.—Heptane sulfochlorination induced by γ-rays was tried by Henglein & Url (52) who found a chain reaction with a high yield. The results were promising for industrial application. Addition of CCl_4 to vinylbutylether has been successfully carried out by irradiation with γ-rays [Nikitina *et al.* (53)].

Radiation induced polymerization is still the most successful application of nuclear energy to chemical synthesis. The difficult study of liquid vinyl-monomer polymerization has been continued mainly for acrylonitrile. The kinetics are complex because of polymer precipitation during the reaction and a steady state treatment is not possible. The reaction rate increases during the irradiation and an important after effect is observed several months after the irradiation has been stopped. Bensasson & Bernas (54a) have shown that the departure from the $I^{0.5}$ dependency is due to precipitation of the polymer from the medium. In a second part (54b) they have studied the post irradiation polymerization and attributed it to free radicals occluded in polymer aggregates. Occlusion reduces the termination coefficient and perhaps even propagation. Russian work on radiation polymerization was summarized by Medvedev (55) at the UNESCO Conference on Radio-isotopes. Probably the most interesting result deals with polymerization of ethylene in solutions of methyl alcohol, acetone, cyclohexane, and *n*-heptane. The yields of solid polyethylene are much higher than in the gas phase under similar conditions of pressure and may reach twenty-five fold that of the gas phase yield. This increase is attributed to a sensibilizing mechanism. The polyethylene obtained differs from polyethylene produced by usual chemical methods. Although this paragraph does not deal with

aqueous solutions, research on the x- and γ-ray initiated polymerization of acrylamide in aqueous solution (56) is related to the work described above. Polyacrylamide has the advantage of being soluble in water and, consequently, no unusual kinetic effects are to be expected because of heterogeneity. Dainton & Tordoff (57) found that the polymerization rate is proportional to the square root of the dose rate. Termination by mutual reactions between growing chains is assumed. The kinetic results are in accord with those of the photochemically initiated polymerization, and it justifies the assumption of a uniform distribution of growing radicals. However the dose rate dependence remains unexplained. An after effect was observed, as in the case of acrylonitrile polymerization, and has been studied in detail for the hydrogen peroxide photosensitized reaction. Dainton & Tordoff make the hypothesis of a polymer radical which might go through several cycles of "burial" and re-emerge before being ultimately terminated. The inactive "buried" phase might be caused by tautomeric changes rather than have a physical origin such as occlusion.

Polyester resins which are solutions of unsaturated polyesters in vinyl monomers are converted by radiation-induced copolymerization into a hard material with a cross linked three dimensional structure. Initiation occurs predominantly on polyester molecules and the G value is probably of the order of 300 to 400 [Charlesby & Wycherley (58)].

A summary on polymerization by high energy radiation appeared in Japan by Okamura *et al.* (59).

ORGANIC AND INORGANIC SOLIDS

Radiation effects on solid polymers.—A recent summary on macromolecules and ionizing radiations was published by Chapiro (60). Ionizing radiation leads to important structural modifications on polymers. This action is entirely specific and cannot be obtained by any other means. It is well known that the radiation resistance varies greatly from one polymer to another. For example, a slight coloration will appear for a dose of 10^{10} rep on polystyrolene while 10^8 rep will be sufficient to change methyl polymethacrylate or teflon to the powdered form.

Degradations of polymethyl methacrylate and polystyrene were studied by Wall & Brown (61). When polymers contain at least one hydrogen atom in the α-position to the CH_2 group, cross-linking is induced by radiation. Both cross-linking and degradation were observed by Wippler (62) on polyvinyl chloride, and by Pearson (63), on polyethylene oxides. A great deal of research was devoted to the properties of irradiated polyethylene. When irradiated, cyclization occurs in high density polyethylene. Infrared spectra presenting a peak at 10.1 μ were interpreted as cyclization of $2(-CH{=}CH-)$ by Dole *et al.* (64). Melting behavior (65), gas formation (66), induced conductibility (67) in irradiated polyethylene are still being studied. The increase in the conductibility which has been observed for a number of irradiated polymers might be due to ions which are trapped in

the polymer. Conductibility changes in several polymers during and after irradiation have been measured (68). An ionic theory of radiation-induced cross linking was published by Weiss *et al.* (69). The use of nuclear magnetic resonance in research on the properties of irradiated polymers has provided some evidence for trapped electrons and free radicals in teflon (70) and polyethylene (71, 72).

Glegg (73) has measured the viscosity in cupriethylenediamine of wood cellulose irradiated with γ-rays. When the sample was irradiated in air or oxygen, an after effect was observed and was more pronounced when the sample was stored in dry oxygen. The after effect is attributed to a further degradation caused by interaction of free radicals and absorbed oxygen.

It is well known that oxygen induces the formation of peroxides from many irradiated organic substances. Chain reactions are initiated which can be observed only when oxygen is present. For example, the irradiation of chloroform gives rise to the formation of a peroxide, CCl_3OOH, which was identified by Schulte *et al.* (74). Durup (75) has observed that polystyrolene in diluted solutions of chloroform was peroxydized in the presence of air. The degradation continued after the irradiation and could be inhibited by β-naphthol and ethanol.

The effects of ionizing radiations on polymer solutions and the radiation induced graft copolymerization are subjects of great interest for industrial application. Research on this subject has been recently reviewed by Chapiro (76). Grafts can be obtained in two ways: (*a*) the copolymer is formed by irradiation of a polymer in contact with a monomer. (*b*) The polymer is preirradiated in presence of oxygen and contact with a monomer follows the irradiation. The first method is used if the polymer is very radiosensitive and the monomer resistant to radiation. The second one is applicable when the monomer is more radiosensitive than the polymer.

The properties of these radiation-induced copolymers are not well known. Chapiro (77) has studied the swelling in dimethylformamide of graft copolymers of acrylonitrile on polyethylene. Swelling becomes important at 110°. Osmotic pressure was measured by Henglein & Schnabel (78). The swelling in several solvents of nylon previously cross-linked by irradiation, was observed by Valentine (79). Research on grafts produced by γ-rays was carried out by Chen *et al.* (80).

Irradiation of glasses.—Hines (81) has bombarded glass with positive ions of argon of 33.5 Kev. From changes observed in the reflection coefficient, one could evaluate that a layer of thickness 0.095 μ was altered. The magnitude of the positive ion flux (5.10^{16} ions/cm^2) is greater than the flux of primary "knocked on" atoms produced by fast neutrons in a reactor.

Borosilicate glasses were irradiated with 2 Mev electrons by Gross (82). The irradiation introduces space charges into the dielectric. Negative charges are concentrated in a layer of arrested electrons at about 0.4 cm beneath the surface. Positive compensation charges are very close to the reverse (unirradiated) face. A complete discharge occurs only at high temperatures.

Radiation chemical changes in inorganic solids.—Decomposition of solid sodium azide by x-rays yields nitrogen gas, ammonia, and hydroxyl ions when the irradiated crystals dissolve in water (83). Heal (84) has tried to determine the nature of the primary product in the crystal which turns brown during irradiation between 50° and 100°. Irradiation of sodium azide dissolved in liquid ammonia produces a blue color which indicates either sodium atoms or trapped electrons, both of which give rise to solvated electrons. Experiments in which samples of sodium azide partially decomposed by irradiation were dissolved in concentrated mercuric chloride solutions show some precipitation of mercurous chloride. It seems, therefore, that the net reaction of decomposition might be $NaN_3 \rightarrow 3/2\ N_2 + Na$ and $N_3^- \rightarrow 3/2\ N_2 + e$. No nitride ions were found. It is suggested that azide radicals are formed by the direct effect and by thermal activation of trapped excitons which afterward decompose.

Radiolysis of solid nitrates by γ-rays was studied by Hochanadel & Davis (85), yielding nitrites and oxygen, as was the case for pile radiation and photochemical decomposition. Nitrate ions were decomposed into NO_2^- and oxygen atoms which either recombine with NO_2^- or react with adjacent NO_3^- to produce NO_2^- and molecular oxygen. It was found also that potassium and cesium nitrates are much more sensitive than, for example, sodium and lithium nitrates. The explanation is the same as in photochemistry; the most sensitive nitrates are those where a greater space is available in the crystal. Instead of comparing the radiation yield G and the quantum yield ϕ the agreement is better when comparison is made between ϕ and G', where G' is equal to G divided by the ratio of electrons in the nitrate ion to the total number in the salt. The improved agreement suggests that the energy imparted to the electrons of the cation is less effective for NO_3^- decomposition than the energy imparted to nitrate ions or to hydration-water electrons.

HOT ATOM CHEMISTRY

Reactions activated by nuclear processes in the gas phase have been studied by Willard (86) by means of gas chromatographic analysis. Reactions between gaseous organic molecules and the product atoms of Cl^{37} (n, γ) Cl^{38}, Br^{79} (n, γ) Br^{80}, I^{127} (n, γ) I^{128} give interesting results with relation to ionizing radiation induced mechanisms. By the addition of inert gases to remove kinetic energy, the authors have found evidence that ion-molecule reactions similar to those observed in mass spectrometry and radiation chemistry might occur.

Radioiodine in neutron irradiated periodate was found mainly in the iodate fraction. Minor activities were isolated as $I^- + I_2$ (87). If the solid was heated before being dissolved, the iodine-iodide activity disappeared below 100°. The retention in periodates increased on heating. The same type of research was carried out for radioactive bromine resulting from the Szilard-Chalmers effect on potassium bromate (88).

WATER AND INORGANIC AQUEOUS SOLUTIONS

Among various objectives in studies of the radiolysis of aqueous solutions is the identification of intermediates and the measurement of their yields. In several studies the choice of various inorganic solutes was made for the purpose of elucidating the primary processes of radiolysis of water. Our understanding of the basic mechanisms of water radiolysis is still incomplete; it is generally assumed that the absorption of energy results in the formation of OH radicals and solvated electrons or H atoms. Molecular hydrogen and hydrogen peroxide are produced, but it is difficult to decide whether they result from the pairwise combination of H and OH radicals formed in regions of high density of energy dissipation (ion *spurs*), or whether they are formed in an earlier step by interaction of excited water molecules, as was proposed by Johnson & Weiss (89): $2H_2O^* \rightarrow H_2O_2 + H_2$, $2H_2O^* \rightarrow H_2 + 2OH$. Moreover, the mechanism by which radicals are produced from ions is still in doubt. (*a*) A number of ion species might be produced by electrons of low energies (10–20 ev). Their neutralization would give rise to various radicals, the proportion of which is not very well known for a condensed phase [see Laidler (90)]. (*b*) The fate of the electron ejected in the ionization act is not known. The electron may be drawn back to the positive ion in order to produce an excited molecule, or it may have quite a long life before it is solvated and dissociates a water molecule. Several years ago Samuel & Magee (91) developed a model based on the first hypothesis assuming recombination of ion pairs and further dissociation into H and OH radical pairs. Radicals in fairly high local concentration were supposed to be formed in ion *spurs*; these radicals then diffuse and combine. In order to elaborate a radical diffusion model which includes competition of the solute-radical reaction with radical combination, it was necessary to investigate quantitatively the behavior of a system of N particles initially inhomogeneously distributed in space. This cannot be accomplished without mathematical approximation if N is larger than 2. Monchick *et al.* (92) have introduced a type of approximation which simplifies the equations. They claim that the radical-diffusion model (with this approximation) is able to explain the main experimental results obtained for aqueous solution radiolysis. On the other hand, the possible existence of a stable bound state of the electron in H_2O was investigated, but Hochanadel (94) could not confirm the interesting result of Jortner & Stein (93) on evidence of electrons in water.

Secondary processes: Water-decomposition yield.—Whatever may be the actual mechanism of the primary processes, hydroxyl radicals, hydrogen atoms, hydrogen, and hydrogen peroxide are assumed to be formed. Their respective yields ($G_p(OH)$, $G_p(H)$, $G_p(H_2)$ and $G_p(H_2O_2)$) depend upon the reactivity and concentration of solute and also upon the density of energy release along the particle track (linear energy transfer LET). We might put forward the following tentative values for 0.8 N sulfuric acid decomposition by various types of radiation (Table I). These values were chosen mainly from Schuler & Barr's (95) study with helions and deuterons, and from

Lefort's results obtained with polonium α-rays, cobalt γ-rays, and soft x-rays (96) on various deaerated solutions of reducible ions (ceric, bichromate, etc.). It seems important to note that in many cases dissolved oxygen scavenges hydrogen atoms from the *spurs* and reduces formation of molecular H_2.

TABLE I

YIELDS OF WATER RADIOLYSIS (0.8 H_2SO_4)

Radiation	LET in ev/Å	$G(H)$	$G(OH)$	$G_p(H_2)$	$G_p(H_2O_2)$	$-G(H_2O)$
Co⁶⁰ γ	0.02	3.65	2.95	0.45	0.80	4.55 ± 0.15
10 Kev. x-rays	0.4	2.90	2.20	0.65	1.0	4.20 ± 0.15
8 Kev. x-rays	0.5	2.55	1.90	0.70	1.05	4.0 ± 0.15
18 Mev. deutrons	0.52	2.40	1.70	0.70	1.05	3.80
8 Mev. deutrons	1.0	1.70	1.50	1.05	1.15	3.80
32 Mev. helions	2.25	1.30	1.10	1.15	1.25	3.60
5.3 Mev. heα(Po)	14.0	0.55	0.65	1.70	1.65	3.95 ± 0.15
B¹⁰(n, α)Li recoils	25.0	0.25	0.45	1.65	1.55	3.55

The determination of free radical and molecular products in sulfuric acid heavy water solutions was carried out by Mahlman & Boyle (97), who found higher yields (by about 10 per cent) than for ordinary water, which agrees with previous results from other authors. Phung & Burton (98), on the contrary, have calculated smaller values for $G(D_2)$, $G(OD)$, and $G(D)$ than for corresponding ordinary water yields. Little work has been carried out on pure neutral water since Hochanadel & Lind's review (99), where the assumed data were $G_p(H_2) = 0.45$, $G_p(H_2O_2) = 0.8$, $G_p(H) = 2.75$ and $G_p(OH) = 2.05$. In his study on the oxidation of phosphite ions by γ-radiation, Cottin (100) found $-G(H_2O) = 3.65$ and $G(H_2) = 0.45$ at a pH value of 4.3, in agreement with the preceding figures.

It can be seen from Table I that $-G(H_2O)$ is definitively smaller for larger LET. However, the yield does not vary with LET, over the range 2.25 to 25 ev/A. In the same range $G(H_2)$ increases by about 0.5. Schuler & Allen (101) have noted this discrepancy between $G(H_2)$ and $G(H_2O)$. It might be that in dense radical tracks, a supplementary process of water decomposition comes into play and counterbalances the increased recombination of radicals due to higher densities. Such a process was proposed for tracks of alpha particles by Lefort (102) in 1954, suggesting that the reaction $H_2O^+ + e \rightarrow H_2 + OH$ occurs when the field in the track column is high enough to draw the electron back to the positive ion. In the same paper it was also assumed that intratrack reactions such as $OH + H_2O_2 \rightarrow HO_2 + H_2O$ take place in local regions of high radical concentration during the expansion of the track. Hart (103) and Donaldson & Miller (104) have proposed the introduction of HO_2 as a primary product of the irradiation. However,

$G(HO_2)$ depends on the relative concentration of H_2O_2, OH, and of any solute which might react with H_2O_2 within the track volume. Its value was found to be much larger for pure water than for solutions containing, for example, ceric ions which react rapidly with H_2O_2.

The values of $G_p(H_2O_2)$ and $G_p(H_2)$ which are indicated in Table I, for polonium α-rays, are upper limits; they are observed when the three "intra-track" back-reactions (i) $H_2O_2 + OH \rightarrow HO_2 + H_2O$, (ii) $H_2O_2 + H \rightarrow H_2O + OH$ and (iii) $H_2 + OH \rightarrow H_2O + H$, do not occur at all, because of the presence of very efficient scavengers for both OH radicals, H atoms, and (or) H_2O_2 (such as, for example, ceric-thallous ions). On the contrary, when one or all of these back-reactions arise to some extent, much smaller yields were found, and we might estimate that $-G(H_2O)$ could decrease from 3.95 to 3.4, $G(H_2O_2)$ from 1.65 to about 1.2, whereas $G(H_2)$ decreases only slightly from 1.7 to 1.55, the rate of reaction (iii) being much smaller than rates of reactions (ii) and (i).

In order to measure $G_p(OH)$ and $G_p(H_2O_2)$ for polonium α-particles, very dilute solutions of ferrous sulfate (in 0.8 N H_2SO_4) were irradiated by Lefort (105). At low concentrations the rate of ferrous ion oxidation by H_2O_2 is known to be so slow that the reaction can be neglected. Such an observation was made by Dainton & Sutton (106) who measured the oxidation produced by accumulated H_2O_2 after the γ-irradiation had been cut off. Lefort has carried out the same sort of experiment with α-rays and deaerated solutions. It is possible to determine the yield of OH radicals which may directly oxidize ferrous ions, or react with H_2O_2 to yield HO_2 (which oxidizes one ferrous ion at low concentrations of Fe^{++}). The value of 0.95 which was found could be written $G(OH)$ in the usual way, or $G(OH) + G(HO_2)$, if Miller's (104) notation is adopted. If (HO_2) is considered as a primary product, $G(-H_2O)$ is equal to $2G(H_2O) + 2G(HO_2) + G(OH)$.

It is now established that for any type of radiation, and particularly for cobalt γ-rays, the so called "molecular" yields, $G(H_2)$ and $G(H_2O_2)$ depend upon the reactivity and concentration of solute. The competition between scavenger reactions and radical combinations during the expansion and diffusion in the *spurs* has been studied in the past both by theoretical calculation and by experiments with various solutes. Similar research was carried out in 1957 by Sowden (107) who found that $G(H_2)$ is decreased by high concentrations of nitrate ions in pile radiation. Acrylamide was claimed to be an appropriate solute to use in measuring $G_p(H_2)$ and $G_p(H_2O_2)$ because it does not react with hydrogen or hydrogen peroxide and is known to be a very efficient scavenger for OH radicals [Collinson et al. (108a)]. When the concentration of acrylamide was varied from 10^{-6} to 10^{-3} M, $G(H_2O_2)$ rose to a maximum of nearly 0.9, the increase being due to an increase in the proportion of free radicals captured by the monomer. The value of $G(H_2O_2)$ subsequently fell to 0.25 in 0.4 M, monomer solutions because of reactions of acrylamide with OH radicals concentrated in *spurs* (radicals which would otherwise induce the formation of H_2O_2). The shape of the second (falling)

part of the curve was very similar to that calculated by Schwarz (109). Collinson *et al.* (108b) have reported preliminary results which indicate that acrylamide in 0.5 M concentration also traps a proportion of "molecular" hydrogen *precursors*. Since evidence was found that $Fe^{3+}OH^-$ ions terminate polymer chains very efficiently, measurements of the yield of ferrous ion led to an evaluation of 6.9 for $G(OH)+G(H)$ for 50 kv x-rays, a value which is higher than that which is generally accepted (4.8 for neutral water and 6.6 in $0.8N$ H_2SO_4). A decrease of $G_p(H_2O_2)$ was also observed by Pucheault & Ferradini (110) who have irradiated solutions of vanadate ions (V^v) with γ-rays. The reduction yield was diminished almost to zero by addition of a sufficient concentration of vanadyl ions (V^{iv}), which react with OH radicals and inhibit combination to H_2O_2. Similar results were obtained by Lefort (96) on solutions of ceric ions containing 10^{-1} M Br^- ions. Barr (111) observed that the addition of 1 M Br^- ions resulted in the oxidation of cerous to ceric ion when irradiation was carried out with 30 Mev helium ions. This oxidation accounts for a decrease of the molecular yield which is assumed to be above 1.25 for this radiation and which was lowered by slightly more than 50 per cent by 1 M Br^-. Dolin & Broucentseva (112) found that Br^- could inhibit $G(H_2)$ in deaerated water. Free bromine was said to be accumulated in the *spurs* where it reacts with *precursors* of molecular H_2.

Another way to change the relative proportions of molecular to radical yields, is to use the same type of radiation and the same solute, but with a dose rate high enough to produce an overlapping of *spurs* and tracks. This will increase combination processes and decrease radical-solute reactions. Such a procedure was attempted with ferrous sulfate solutions irradiated at 10^{10} rads/sec. $G(Fe^{+++})$ was not much changed, although a small decrease ($G=14.3$ for 4 Mev electrons) was observed by Keen (113) who concluded that the difference between this value and Schuler & Allen's result at dose rates lower than 10^6 rads/sec. (15.45) was not significant.

It becomes more and more evident that the water-decomposition yield by gamma radiation is higher when the solutions are acidified with H_2SO_4. On the other hand, the yield is not dependent on the acidity for high ionization-density particles. This interesting problem was pointed out by Allen in 1954 (114). A reaction such as $OH+HSO_4^-\rightarrow OH^-+HSO_4$ was proposed, and it was suggested that the HSO_4 free radical does not necessarily behave as an OH radical. Recombination processes might be slower for HSO_4 radicals and H atoms than for OH radicals and electrons. Some time ago Weiss (115) proposed another hypothesis according to which $G(H_2O)$ would be higher in acid medium because of interaction of H_3O^+ and OH radicals inside clusters. $H_3O_2^+$ ion radicals would be formed which then decompose into $H_2O_2+H^+$. $G(H_2O_2)$ is thereby higher in acid solutions than in neutral media; this does not explain why $G(OH)$ as well is higher in acid medium.

Radiation induced chemical reactions for inorganic solutes.—The production of hydrogen peroxide in aerated water has been extensively studied for several years. Very little work, however, was carried out on alkaline water solutions. A paper has appeared on the influence of pH on H_2O_2 production

in aerated solutions [Koulkès-Pujo (116)]. Unfortunately, measurements were not made for initial yields but for doses at which secondary reactions were already very important. The sharp decrease in $G(H_2O_2)$ which occurs when pH values change from 2 to 3, observed by Bonet-Maury & Lefort (117) in 1950 has been confirmed and attributed to HO_2 dissociation into O_2^- and H^+ (116). A small increase in yield was found for pH 11.7 and a further decrease for pH higher than 13.35. It was explained by dissociation of H_2O_2 into HO_2^- and H^+ and of OH into O^- and H^+. Decomposition of 10^{-4} molar H_2O_2 by γ-radiation, in heavy and ordinary water, was measured by McDonell (118). $G(-H_2O_2)$ was higher for heavy water (4.1 compared with 3.6). The explanation depends on the assumption of a higher yield for radical production from heavy water. Baxendale & Wilson (119) have confirmed that the quantum yield for the photolysis of H_2O_2 at 2537 A is equal to 1.00 at high light intensities.

Several chemical studies of interest for radiation chemistry and for OH radical properties were carried out. The rate constant of the reaction between Fe^{++} and H_2O_2 in acid solutions was redetermined (120). It was found to be independent of the concentration of perchloric acid

$$\left(k_0 = 5.3 \times 10^8 e - \frac{9450}{RT}\right),$$

but to increase slightly in sulfuric acid concentrations above $10^{-2}N$.

$$\left(k_0 = 9.6 \times 10^8 e - \frac{9750}{RT} \text{ in 0.8N } H_2SO_4\right).$$

The reactivity of hydroxyl radicals in aqueous $HClO_4$ solutions was studied by Dainton & Hardwick (121). They found that the reaction H_2+OH is about 7 times less rapid than $Fe^{++}+OH$, whereas the latter is 2.6 times less rapid than $CO+OH$. The reactions of OH with dissolved hydrogen and carbon monoxide are important in radiation chemistry, since H_2 and CO are retarding agents for radiation induced oxidations in acid deaerated solutions.

Oxydo-reductions.—From our general knowledge of the mechanism of water radiolysis into OH radicals, H atoms and H_2O_2, we might be able to predict very qualitatively the behavior of any solute under radiation, if its redox properties are known. The usual stationary state kinetics for the intermediates is not applicable, especially if the rate of the global reaction is controlled by reactions between radicals. However, Schwarz & Allen (122) have shown that an equivalent treatment could be applied if the number of radicals at a given dose is considered instead of their concentration. It is therefore possible to predict whether a solute will be oxidized or reduced when its reactivities towards OH, H, and H_2O_2 are known and if $G(OH)$, $G(H)$, and $G(H_2O_2)$ have been determined.

(a) Very reducible ions (redox potential[3] higher than $E_0 = +1.0$ v) will

[3] Redox potentials on the hydrogen scale use the European convention with respect to sign.

be reduced by H and H_2O_2 whereas the reduced form will be oxidized by OH radicals. Oxygen has no effect since HO_2 radicals are equivalent to H atoms. The reduction of ceric ions (H_2SO_4, $0.8N$) is now a classical example for which $G(Ce^{3+})$ is equal to $G(H)+2G(H_2O_2)-G(OH)$. On the addition of other solutes which are able to change OH oxidizing species into reducing intermediates, $G(Ce^{3+})$ is increased to $G(H)+2G(H_2O_2)+G(OH)$. Formic acid, thallous ions, and benzene produce such an increase. The reaction has recently been studied, for irradiations with cobalt γ-rays, 10 and 8 kv. x-rays (96), 220 kv. x-rays (89) and with helium ions at various energies (95). Table II is taken from the publications of Lefort and Johnson & Weiss.

TABLE II

RADIATION-INDUCED REDUCTION OF CERIC AND OTHER IONS IN $0.8N$ H_2SO_4

Radiation→	Co^{60} γ	220 kv x-rays	10 kv x-rays	8 kv x-rays	5.3 Mev α-particles
$G(Fe^{3+})$ air	15.6	15.5	14.15	13.4	5.6
$G(Ce^{3+})$	2.4	3.15	2.7	2.9	3.2
$G(Ce^{3+})$ Benzene	8.2		8.0		4.2
$G(Ce^{3+})$ Formic acid	8.15	8.5			
$G(O_2)=G(H_2O_2)$	0.8	1.07	1.0		1.6
$G(H_2)$	0.45	0.57	0.65		1.6

In the radiolysis of sulfuric acid solutions containing ceric ion-cerous ion-formic acid mixtures, Spencer & Rollefson (123) have found that at constant $(Ce^{3+})/(HCOOH)$ the initial $G(Ce^{3+})$ decreased with decreasing total concentration of cerous ion and formic acid, whereas $G(Ce^{3+})$ is independent of thallous ion concentration which, otherwise, has the same quantitative effect. Sworski (124) has studied this problem and concluded that a quantitative interpretation is possible if we assume that OH radicals react with H_2SO_4. This hypothesis has already been suggested by Allen (114). Cerous ion, formic acid, and sulfuric acid would therefore compete for an OH radical. It is assumed that the HSO_4 radical oxidizes Ce^{3+} as well as OH does but does not react with formic acid. Furthermore, the dependence of $G(Ce^{3+})$ on sulfuric acid concentration was demonstrated by experiments with 4.0 M sulfuric acid solutions containing ceric ions where either thallous ions or formic acid were added. This influence of H_2SO_4 might be extended to other systems. If HSO_4 radicals are formed, it seems reasonable to assume that they would not always react as do OH radicals. For organic solutes a reaction such as $RH+OH \rightarrow R^{\cdot}+H_2O$ might be much more probable than $RH+HSO_4 \rightarrow R^{\cdot}+H_2SO_4$ since the H—OH bond is much stronger than the H—HSO_4 bond. Sworski (125) has also carried out a study on the photolysis of ceric ion-thallous ion mixtures in H_2SO_4 aqueous solutions. Tl^+ competes with cerous ion for reaction with an OH radical produced by the photochemi-

cal process $Ce^{4+}+H_2O\rightarrow Ce^{3+}+H^++OH$. Preliminary results on the gamma radiation-induced reduction of thallic, cobaltic, and chromate ions in sulfuric acid solutions are very high, similar to those obtained with ceric ions (96). The addition of benzene increased the yield to 8.2 for all of these solutes.

Sworski's experiments (126) on mixtures of Cr^{vi} and Tl^+ have shown that chromic ion concentrations up to 10^{-2} M have no measurable effect on $G(Cr^{3+})$, a result which could be explained if the OH radical does not oxidize chromic ion but disappears by oxidation of the intermediate Cr^v or Cr^{iv} ion. From preliminary experimental results published by Pagès et al. (127), it seems to the author of the review that the mechanism of the reduction of Pu^{vi} to Pu^{iv}, in sulfuric acid solutions, is similar to that outlined above, although the possible formation of a peroxide on Pu^{iv} and the slow rate of reduction of Pu^{vi} by H_2O_2 might bring some very different quantitative results. Both HSO_4^- and H^+ concentrations were found to have an important influence. The self reduction of Am^v and Am^{vi} in $HClO_4$ solutions was studied by Hall & Markin (128) but the processes are complicated by the disproportionation of Am^v. Reduction by γ-rays of V^v to vanadyl ions was studied by Pucheault & Ferradini (110). $G(H_2)$ and $G(-VO_2^+)$ were about the same as for ceric ions. However, it could be shown that "molecular" H_2O_2 reacts via the reaction $H_2O_2+OH\rightarrow HO_2+H_2O$ (i), as long as the concentration of V^{iv} is small enough. The redox potential is indeed much lower ($E_0 = +1.0$ v) than for the ceric-cerous system, and H_2O_2 does not reduce the oxidized form. When the concentration of V^{iv} was higher than $2\cdot 10^{-2}$ M the reduction yield was lowered from 2.7 to 1.8 because all available OH radicals were scavenged and reaction (i) was inhibited. Hydrogen peroxide was therefore accumulated in the solution and subsequently reacted with V^v yielding pervanadate (VO_4^-). The yield for the disappearance of VO_2^+ is therefore equal to $G(H)-G(OH)+G(H_2O_2)$ instead of $G(H)-G(OH)+2G(H_2O_2)$, and $G(VO_4^-)=G(H_2O_2)$.

Two exceptions were found to the above general mechanism. In both cases reduction yields were much greater than the preceding values, and it was shown that OH radicals do not oxidize the reduced form. Polyvanadate ions at pH = 2 were reduced by γ-rays with a yield of 5.5 (110), and permanganate ions were reduced in sulfuric acid solutions with various yields, depending on HSO_4^- concentrations which were generally higher than 8.2 equivalents per 100 ev, both in the presence and absence of oxygen. It has been assumed by Simonoff (129) that OH radicals and MnO_4^- ions compete for manganous ions produced by the radiation. Under some conditions almost all Mn^{++} ions were reoxidized to MnO_2 by MnO_4^-. Remaining OH radicals combined to form H_2O_2 which reduced other MnO_4^- ions. As expected benzene was found not to enhance the reduction yield.

(b) When the redox potential is lower than about $E_0 = +1.0$ v, hydrogen peroxide is no longer a strong reducing agent and may either oxidize the reduced form of the system, or react with OH radicals to yield HO_2. Depending on pH, HO_2 or O_2^- may be an oxidizing or reducing agent. We might expect radiation induced equilibria as were found for nitrite and nitrate (130). For

aerated acid solutions H atoms are transformed into HO_2 and the oxidation yield is much higher than in vacuo. Many years ago Fricke & Hart (131) found that potassium ferrocyanide was oxidized in vacuo with a yield of 0.9 which might be calculated as $G(OH) - G(H) + 2G(H_2O_2)$. This study has been reopened by Tarrago et al. (132). In a preliminary note, a low yield of 0.95 was confirmed for deaerated acid solutions. In presence of oxygen it was found that reduction of ferricyanide could occur at pH values higher than 10. For freshly prepared acid solutions, initial yields of the order of 7, corresponding to $G(OH) + G(HO_2)$, were obtained. An observed after effect was probably due to the slow reaction of ferrocyanide with H_2O_2 formed during the radiolysis.

The radiation-induced oxidation of uranous sulfate in deaerated aqueous solutions ($3N$ H_2SO_4) is classical [Haïssinsky & Duflo (133)]. The yield becomes independent of the concentration of uranous salt only at a rather high concentration ($5 \cdot 10^{-2}$ M). A semiempirical calculation, similar to previous calculations applied by Lefort to the effect of concentration on the oxidation of fluoresceine leucobase (130), was found to fit the experimental curve. It was assumed that OH radicals and H_2O_2 oxidize U^{iv} to U^{vi} and that H atoms recombine into H_2 without reacting with the solute. When the concentration of uranous sulfate was sufficient to scavenge all OH and H_2O_2, $G(U^{vi})$ was equal to 2.05 and therefore $G(-H_2O) = 4.1$. This decomposition yield of water is smaller than the accepted value of 4.55 in $0.8N$ H_2SO_4. However, contradictory results were published by Firsow & Erschler (134), who claimed that U^{vi} was reduced by H atoms during the radiolysis at the same time as U^{iv} was oxidized. If such a reduction occurs, it explains why the above calculation yields small values. When oxygen was present in the solution, initial G values as high as 18 were measured by Haïssinsky & Duflo. The yields were dose rate dependent. If oxygen was not supplied to the solution at a sufficient rate, the yield decreased rapidly. A chain mechanism was necessary to explain the results. The chain is presumably initiated by oxidation of U^{iv} to the intermediate valency of five (UO_2^+) via OH and HO_2 radicals. The chain is propagated by transfer of one electron from UO_2^+ to O_2. In acid medium O_2^- is transformed to HO_2.

(c) For several readily oxidizable species oxidation yields in the absence of oxygen are often much higher than $G(OH) + 2G(H_2O_2) - G(H)$. H atoms not only reduce the oxidized form but sometimes enter into an abstraction reaction which is equivalent to an oxidation. Cottin (100) has shown that such a mechanism was responsible for the oxidation of deaerated solutions of phosphites by γ-rays at concentrations for which the dilution effect was already obtained. Cottin has assumed that both OH radicals and H atoms could produce the intermediate HPO_3^-. The reaction $H_2PO_3^- + H \rightarrow HPO_3^- + H_2$ was said to be possible because bond energy of H—H is much higher than that of H—HPO_3^-. A similar type of reaction will be discussed below for organic compounds. Oxidation yield is therefore equal to $G(OH) + 2G(H_2O_2) + G(H)$ since H_2O_2 might oxidize also HPO_3^-. When oxygen was

bubbled through the solution, a chain reaction was propagated via an electron transfer from the intermediate HPO_3^- to an oxygen molecule:

$$HPO_3^- + O_2 \rightarrow HPO_3 + O_2^- \qquad\qquad 1.$$

In acidic medium O_2^- is neutralized to HO_2 and carries on the chain by the reaction

$$HO_2 + H_2PO_3 \rightarrow H_2PO_4^- + OH \qquad\qquad 2.$$
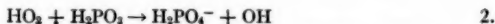
In neutral solutions reaction (1) was assumed to be favored and reaction (2) to be inhibited by electrostatic repulsion. Oxygen consumption measurements provided evidence for this mechanism. Oxidation yields as high as 48 equivalents per 100 ev were obtained in neutral solutions. Experiments were also carried out by Cottin on the effect of polonium α-rays on sulfuric acid solutions of phosphites. For an initial concentration high enough (10^{-2} M), a G value of 0.94 was attained for $(H_2PO_4^-)$, whereas 1.75 was obtained for $G(H_2)$. Since $G(O_2)$ was found to be 0.42 and $G(H_2PO_4^-)$ was equivalent to $G(H_2O_2)$ obtained in pure sulfuric acid solutions, we might suggest that intratrack reactions (which yield O_2) are of the same magnitude in pure water and with added phosphite. It would indicate that H_2O_2+OH and HO_2+HO_2 are much more rapid than any of the reactions of one of the phosphorous compounds with H_2O_2, OH, or HO_2.

(d) Ferrous ion oxidation has been extensively studied for many years. The high yields observed in absence of oxygen and the low value of the ratio

$$R = \frac{G(Fe^{+++}) \text{ in } O_2}{G(Fe^{+++}) \text{ in vacuo}} = 1.9$$

were explained by Weiss's hypothesis; i.e., formation of H_2^+ which oxidizes ferrous ions in absence of air (135). However, evidence for the existence of H_2^+ was not found in the study of the radiation-induced oxidation of ferrocyanide ions (132) and uranous ions (133). Experiments on ferrous ions in acid solutions in which H atoms would be produced in an unambiguous manner would be very desirable. Two papers have appeared on the action of atomic hydrogen on polarized electrodes (136) and on the redox properties of atomic hydrogen diffusing to the polarized electrode surface (137). Both favored the conclusion that H atoms, adsorbed at the surface, might show oxidizing properties only when the overvoltage of the electrode is high enough; in such cases the diffusion of atomic hydrogen would decrease the overvoltage. At low overvoltages, on the other hand, atomic hydrogen increased overvoltage, and therefore acted as a reducing agent.

Schwarz (138) has studied the action of γ-rays on aerated solutions of ferrous chloride (HCl 0.4 M). Ferric ion production was not linear with absorbed dose although the initial yield was the same as for sulfuric acid solutions. The falling off in yield as the reaction proceeds was attributed to competition between ferric ions and oxygen for H atoms. This competition is usually neglected in sulfuric acid solutions because reduction of the $FeSO_4^+$

complex by H atoms is rather slow. From kinetic calculations Schwarz has shown that $k_{Fe^{+++}}/k_{O_2} = 0.004$, $k_{FeCl^{++}}/k_{O_2} = 0.23$ and $k_{FeCl_2^+}/k_{O_2} = 0.48$.

Proskurnin et al. (139a) claimed some years ago that in oxygenated solutions, the yield of oxidation of ferrous sulfate by γ-rays could reach $G = 60$ for concentrated H_2SO_4 ($4N$) and ferrous ions (10^{-1} M). It was suggested that this very high yield was due to excitation processes. Orekhov et al. (139b) have carried out photochemical experiments in $H_2SO_4(5N)$. The photochemical oxidation was assumed to yield tetravalent ferrate, which subsequently decomposed into Fe^{++} and O_2. The decomposition was enhanced by boiling and by an excess of Fe^{3+}. For low ferric ion concentrations, the initial rate of ferric ion production was much slower than the rate of ferrous ion disappearance. The authors assumed that complex compound (Fe^{++}, O_2) would be transformed into $Fe^{++} \cdot O{=}O$, only in sulfuric acid. For hydrochloric acid Cl^- destroyed the peroxide which could not be titrated. These experiments might explain why controversial results were published on the radiation-induced oxidation of ferrous sulfate in $4N$ H_2SO_4. It appears that in the future both Fe^{++} and Fe^{+++} should be titrated.

Direct effects.—Direct effects occur on solutes when highly concentrated aqueous solutions are irradiated. The amount of the effect increases with concentration since the absorbed dose in the solute molecules increases with the concentration. Very little work has been reported for concentrated solutions. Cottin (140) has summarized the present situation. His study on perchlorate ions, which are not decomposed in dilute solution, has shown that ClO_4^- yields both ClO_3^- and Cl^- at the same rate over a range of temperature from $-80°$ to $+20°$. The energy necessary to decompose one ClO_4^- ion was 24.7 ev, a value slightly higher than that found by Heal (141) for the energy of decomposition of potassium perchlorate crystals.

Mahlman (142) has measured the rate of nitrite production when concentrated solutions of metal nitrates were irradiated with γ-rays (0.1 to 0.5 M). Elimination of the back reaction which destroyed nitrite was effected by the use of Ce^{iv} ion, which removed reducing radicals and H_2O_2 produced from water. The nitrite yield was taken to be one-half the difference between the observed G values for Ce^{iii} (in 0.8N sulfuric acid) with and without the nitrate present. It was concluded that the yield of nitrite produced by direct action was (a) independent of the cation, a result at variance with the effect on solid nitrates [see above, Hochanadel (85)], (b) dependent on the total absorbed energy regardless of the particular constituents of the solution and (c) dependent on the nitrate concentration. The direct action became practically zero at about 0.04 M. Radiation-induced decomposition of molar concentration of $NaNO_3$ in aqueous oxygenated solutions was also studied by Bach et al. (143) who measured the rate of production of NO_2^-, H_2O_2, and O_2. The energy absorbed in water yielded H_2O_2 and O_2, whereas part of the transformation to nitrite was attributed to a direct effect.

Radiation-induced decomposition of concentrated thorium nitrate solu-

tions was studied by Boyle & Mahlman (144). The results are of practical interest since these solutions were proposed as a blanket material in power-breeder reactors. Nitrite ion production was very low although a yield of 2.55 mole. per 100 ev was found when ceric ions were added. The nitrite was therefore removed as it was formed and probably oxidized back to nitrate. Principal final products were H_2, N_2, O_2, and N_2O. When the concentration was 2.73 M, nitrogen G values were found to be 0.06 for fission products, 0.006 for pile radiation, and 0.001 for γ-radiation alone. Such a radiation stability is of importance.

Also of practical interest, was a study by Dolin & Doujenkov (145), who have built a radiation-galvanic cell containing a solution of ferrous and ferric ions in $3N$ sulfuric acid. The cell was separated by a diaphragm through which H^+ ions could migrate whereas iron ions could not. When the cell was irradiated, an electric current could be measured between two platinum electrodes since the electrochemical reactions $Fe^{+++}+e \rightarrow Fe^{++}$ and $H_2 = 2H^+ + 2e$ at the electrodes and were compensated in the solution by the radiation-induced reactions of OH and H free radicals with Fe^{++} and Fe^{+++}.

AQUEOUS SOLUTIONS OF ORGANIC COMPOUNDS

During the past year special efforts were made to elucidate the mechanism of radiolysis of aqueous solutions of ethanol and benzene. Very few investigations have been carried out on ethanol solutions since the measurement of Fricke *et al.* (146) on the hydrogen yield. Several interesting features were found by Weiss *et al.* (147) who measured the amounts of acetaldehyde, hydrogen peroxide, hydrogen, and butane2:3diol for different concentrations and pH values in aerated and deaerated solutions irradiated with 200 kv x-rays. One of the most important results was that the yield of acetaldehyde is never independent of the concentration. The dilution effect which is very often observed for inorganic solutes is rather rare for organic compounds in aqueous solutions as has been shown by many results on amino acids, lactic acid, etc. For oxygenated ethanol solutions, Weiss *et al.* (147) have obtained a curve of acetaldehyde yields versus ethanol concentrations which tends to flatten out at a concentration of 10^{-3} M but increases again at hi her concentrations and attains values which are much greater than the maximum that could arise from hydroxyl radicals resulting from decomposition of water. The authors assumed that in the first place, CH_3CHOH radicals are formed by the action of hydroxyl radicals on ethanol molecules, and that subsequently, peroxyradicals result from the addition of molecular oxygen. The first rising part of the curve is explained by competition between the reaction $HO_2 + OH \rightarrow H_2O + O_2$ and the formation of aldehyde via $CH_3C(O_2)HOH + HO_2 \rightarrow CH_3CHO + H_2O_2 + O_2$. A G value slightly higher than 2 is therefore attained which corresponds to the available amount of OH radicals. This competition is temperature sensitive. For higher concentrations the H_2O_2 yield stays more or less constant until an ethanol concentration of 1 M is reached, whereas the further increase of aldehyde is tentatively attrib-

uted either to competition between $H+O_2\rightarrow HO_2$ and CH_3CH_2OH+H $\rightarrow CH_3CHOH+H_2$, or to electronic excitation of the ethanol molecules by the subexcitation electrons produced by radiations according to the suggestions of Platzman (148) and of Weiss (149). The first explanation would be restricted only to experiments conducted in presence of air while the second is applicable also for vacuum results. Unfortunately, the concentration dependence has been studied *in vacuo* only up to 2.4×10^{-2} M, for which the aldehyde yield is equal to 1.90 and the butane2:3diol G value is 1.65. The sum would lead to $G(OH+H)=3.55$ at pH 1.2, which is a reasonable value. Therefore, since it is assumed by the authors that both H and OH react with CH_3CH_2OH and with CH_3CHOH, there is no need from the energetic point of view of excitation by slow electrons. The dependence on concentration would only signify that a solute concentration of 3 or 4×10^{-3} M is necessary to scavenge all the OH radicals and H atoms available. However, the suggestion that subexcitation electrons have a significant role is of interest since it is well known that ethanol molecules can dissociate easily because of their low excitation and ionization levels. This mechanism might be extended to other organic solutes for which similar concentration effects were observed. The pH dependence of the radiolysis of aqueous ethanol solutions was also investigated. *In vacuo* the hydrogen yield is much higher ($G(H_2)$ $=4.2$) for a pH range of 1.2 to 4 than for pH values greater than 4.5 ($G=2.5$ at pH$=7$). For the same variation of pH the acetaldehyde yield passes from 2 to 0.2. The authors attribute these results to reactions involving the H_2^+ radical-ion, mainly $CH_3CHOH+H_2^+\rightarrow CH_3CHO+H_2+H^+$, although there is no pH dependence between 1.2 and 4 where the equilibrium $H+H^+\leftrightarrows H_2^+$ should be very much displaced. Also of interest was the observation, for air equilibrated solutions at pH$=0.1$ that after a certain absorbed dose, a break occurred in the rate of formation of H_2O_2, owing to the exhaustion of the dissolved molecular oxygen in the solution. Decomposition of H_2O_2 by H atoms which are no longer removed by $H+O_2\rightarrow HO_2$ leads to the formation of OH radicals and therefore to increased attack on the ethanol. It was, indeed, observed that the decomposition of H_2O_2 was accompanied by an increased formation of acetaldehyde. Experiments with evacuated ethanol solutions containing added H_2O_2 have confirmed the above explanation.

It has been established for quite a long time that the radiolysis of aqueous solutions of benzene yields phenol and diphenyl (150). However, the mechanism of the reactions was not elucidated. A recent study by Phung & Burton (98) provided additional data at various pH values. (*a*) In air free solutions it has been shown very clearly that the hydrogen abstraction reaction by H atoms does not occur in significant proportions because H atoms are more readily used up for benzene polymerization ($H+PhH$ $\rightarrow PhH_2\rightarrow$Polymer). Experiments with benzene-d_6 gave an additional proof for such a mechanism. (*b*) Hydrogen peroxide primarily formed by hydroxyl combination was destroyed in neutral solutions via the reaction (*i*) H_2O_2+H $\rightarrow OH+H_2O$, rather than by $Ph+H_2O_2\rightarrow PhOH+OH$, as was already sug-

gested by Baxendale & Magee's experiments with Fenton's reagent (151). Phung & Burton made the assumption that reaction (i) is pH dependent in order to explain that H_2O_2 is observed only in acid solutions. (c) In presence of oxygen, $H+O_2 \rightarrow HO_2$ is followed by $HO_2+HO_2 \rightarrow H_2O_2+O_2$. Oxygen is also consumed by the reaction $Ph+O_2 \rightarrow PhO_2$ and the peroxyradical is subsequently hydrolyzed; $PhO_2+H_2O \rightarrow PhOH+HO_2$. However, the rate of oxygen consumption is about twice that which could be calculated from these two processes. It is therefore assumed that PhO_2 reacts with benzene to give OH radicals and oxygenated products. One of these might be the muconic dialdehyde found by Daniels $et\ al.$ (152). No more information has been obtained about other products, but a short chain reaction is indicated by the O_2 consumption data. The study gave information regarding the primary yields in γ-ray induced decomposition of both heavy and ordinary water. As was noted by the authors, these primary yields are lower than corresponding values obtained with inorganic solutes. This is particularly true for $0.8N$ H_2SO_4 solutions, and the usual increase of $G(OH)$ and $G(H)$ values, when an unbuffered neutral solution is acidified to $0.8N$ H_2SO_4, was not found. It might be suggested that benzene has an effect on the mechanism of sulfuric acid-water radiolysis and suppresses the effect of SO_4^- ions.

One of the interesting questions of radiolysis of organic compounds in aqueous solutions is whether or not the hydrogen abstraction reaction $RH+H \rightarrow R^{\cdot}+H_2$ occurs. We have seen that it is not important for benzene. On the other hand, Weiss $et\ al.$ (153) have observed high yields of hydrogen for several organic solutes, even in presence of methylene-blue, which have to be attributed to dehydrogenation of ethanol, lactate, and formate by H atoms. It seems, therefore, that benzenoid systems are more or less exceptions because hydrogen atoms can react by the addition mechanism. Some other aspects of the reduction of methylene-blue in deaerated aqueous solutions containing an excess of ethanol, lactate, formate, benzoate, d,l,alanine, or phenyl-β-alanine were considered by these authors. Their main conclusion was that methylene-blue can be reduced via the semiquinone radical, both by hydrogen atoms and by RH radicals produced from the added organic compounds. With regard to the intermediate role of the semiquinone radical, Swallow (154) has obtained, by irradiation of methylene-blue in the presence of excess of ethanol in strongly acid solutions, the ultraviolet spectrum of the same stable semiquinone free radical that may be produced by reduction with titanous chloride. The radiation-induced formation of free organic radicals as efficient reducing agents was also extensively studied by Day & Stein (155) in a very careful research on methylene-blue in presence of added ethanol, benzoate, and lactate.

It seems also that thionine decolorization by x-rays presents the same characteristics as decolorization of methylene-blue. Added benzoic acid also leads to a reducing radical [Cabot $et\ al.$ (156)]. Some other studies on the radiation chemistry of dyes in aqueous solutions were made by Chektman & Ratner (157) and by Verechnesky $et\ al.$ (158).

Glucose solutions were irradiated with electrons and x-rays by Bothner-

By & Balazs (159). In neutral as well as in alkaline solutions, acidic products were formed and there was a loss of reducing power. No products could be identified.

A number of other aqueous solutions of organic systems of biological interest have been irradiated. An interesting paper appeared on the synthesis of amino acids by beta radiation (160). When aqueous solutions of ammonium acetate were irradiated, glycine and aspartic acid were formed, probably via reactions between NH_2 radicals and CH_2COONH_4 radicals. Similarly, Vermeil & Lefort (161) have shown that one could induce hydroxylation of phenylalanine by irradiation in neutral aqueous solutions. Ortho, para, and meta tyrosine were produced and identified by paper chromatography as well as deamination products and ammonia.

In comparison with preceding years very little work has appeared on the radiolysis of amino acids. Drake et al. (162) studied the effect of γ-radiation on the amino acid content of insulin; the radiosensitivity of the constituents (cystine, tyrosine, phenylalanine, proline, and histidine) was very great; cysteic acid was formed. The research was carried out mainly in order to provide information on flavors and aroma developed in the sterilization of food proteins by ionizing radiation.

The degradation by x- and β-rays of d,l,methionine, either labeled with S^{35} or inactive, yields homocysteine by demethylation, as well as several acids by deamination and methionine-sulphoxide by oxidation (163); other products were formed which could be observed on chromatograms of irradiated methionine but were not identified.

With relation to radiation chemistry the action of atomic hydrogen on aqueous solutions of cysteine and glutathione was studied by Littman et al. (164). Hydrogen atoms were produced by electric discharge in a stream of hydrogen diluted with helium. The gas was bubbled through the solutions. The equipment was calibrated for atomic hydrogen by precipitation of metallic silver from silver nitrate solutions. The action of hydrogen atoms on aqueous solutions of cysteine produced mainly cystine in acid and neutral solutions. In alkaline solutions the amount of H_2S increased rapidly and that of cystine decreased to zero. Chain reactions were proposed. As for γ-ray radiolysis, there was no indication of any attack on the amino group. Similar results were obtained for glutathione. This approach seems to be very promising for the elucidation of the role of H atoms in water radiation chemistry.

On the other hand the mechanism for the reaction of Fe^{++}, H_2O_2, and glycine in an aerobic aqueous solution was elucidated by Maxwell & Peterson (165). Hydroxyl radicals produced by the Fenton reagent attack the glycine at the amino group.

Radiation effects on aqueous, oxygenated, thiourea solutions were studied with the help of indicator S^{35} by Dale & Davis (166). Free sulfur was liberated with a very high yield and a chain reaction is suggested. Traces of NH_3 and SO_4^{--} were also found. The authors established that H_2O_2 plays no

significant part in the process and that the pH dependence is in favor of an oxidation chain initiated by HO_2 radicals.

With relation to research on the degradation of nucleic acids in aqueous solutions by ionizing radiations, the chemical action of x-rays on α- and β-glycerophosphates was studied in some detail by Scholes *et al.* (167). Both organic phosphates lead to the formation of inorganic phosphate, but a post-irradiation release of inorganic phosphate was observed only for the α-glycerophosphate, owing to the decomposition of labile dihydroxyacetone phosphate. For the β-compound, although there is no after effect, further amounts of inorganic phosphate could be liberated on hydrolysis under special conditions at 100°. The yields of total and inorganic phosphate were much greater *in vacuo* than in presence of oxygen, particularly under acid conditions where the G value rises to 4.9 at pH 1.2. Formaldehyde was formed only if oxygen was present. There are several possible mechanisms for the radiation effects. The results are of interest with regard to the processes involved in the degradation of nucleic acids since it has been shown that a number of ribonucleotides are attached at the level of the sugar components, resulting in a release of phosphate, whereas the formation of hydroperoxides in presence of oxygen is associated with pyrimidine bases.

The biological interest in the action of oxygen and its connection with radiation-induced formation of organic peroxides has given rise to several recent publications. Hydroperoxides were detected in aerated solutions of amino acids and peptides [Okada (168)] and thymine [Eckert (169)] which were irradiated by x-rays. Biological effects of these organic peroxides were studied by Philpot *et al.* (170) and by Latarjet *et al.* (171). It was found that DNA is very sensitive to several peroxides. Daniels *et al.* (172) have shown that in oxygenated solutions of DNA, two different peroxides associated with two different pyrimidine nucleotides were formed by irradiation. The thymine hydroperoxide is relatively stable and might have originated from the saturation of the double bond by addition of an OH and an HO_2 group. The relations between radiation formed organic peroxides, oxygen effects, and radiobiological effects were discussed in a colloquium held in Paris in January, 1957. In the introduction Latarjet made an interesting point regarding the peroxidation of important biological molecules which could be induced both by direct and indirect action. Similarly, Alexander (173) observed that the inactivation of solid trypsin was sensitive to the effect of oxygen when irradiated by γ-rays and not by α-rays. One of the hypotheses suggested is that oxygen molecules capture electrons and lead to O_2^- which inactivates the protein molecules.

Ebert & Swallow (174) have shown that irradiation of aqueous solutions of cocarboxylase (thiamine pyrophosphate) does not affect the phosphate but leads to the same attack of thiazole or pyrimidine chromophores as does thiamine chloride (vitamin B_1). Alcohol is an effective protective agent only in air saturated solutions.

Irradiated ovalbumin was found to be denaturated by urea at a faster

rate than unirradiated material (175). It seems that the irradiation damage to the protein might be the rupture of bonds in hydrogen bond groups.

Dosimetry and Irradiation Facilities

Fricke's dosimeter has been very widely used for several years and agreement seems now complete on the value of $G = 15.6 \pm 0.1$ per 100 ev for the oxidation yield of ferrous sulfate in aerated aqueous solutions of sulfuric acid irradiated by γ-rays or electrons of more than 100 kev. However, absolute determinations were made during the past year for beams of helium ions, deuterons of various energies, and for very high energy electrons. Schuler & Allen (101) measured the beam current absorbed in ferrous sulfate solutions and determined accurately the energy from the mean range of particles in aluminum. They have confirmed previous results and give a series of G values between 6.0 and 11.2 for the absolute yields of oxidation at various helium and deuteron energies. An empirical yield-energy relationship was established which is of great interest both for practical dosimetry and for the study of the yield as a function of rate of energy loss (LET). There was good agreement with the experimental value found for tritium β-rays [$G = 12.9$ (176)] and, on the other end of the scale, with Schuler & Barr's data (177) on the yield for the recoils from the boron (n,α) reaction. $G(Fe^{3+})$ for α-particles of polonium (5.3 Mev) has been previously reported by three different authors as 5.9 to 6.2. A new determination was made by Lefort (105) who found 5.6 ± 0.15, a value which is in agreement with the figure to be expected from Schuler & Allen's measurements made at higher energies.

When 10 to 20 Mev electrons irradiate aqueous solutions, polarization of atoms by the field of the fast particle shields distant atoms and tends to reduce the effective field intensity. The amount of energy loss associated with distant collisions is therefore less in a condensed phase than for the gaseous state. The absorbed dose in rads or ev/gr measured via ionization chambers has to be corrected. When such a correction was effected, Zsula et al. (178) found G values of 15.5 per 100 ev at 6.3 Mev, and 15.7 at 16 Mev. Neglect of the polarization effect would lead to much lower values.

A determination of $G(Fe^{+++})$ for 4 Mev electrons at a dose rate of 10^{10} rads/sec was made by Keen (113). The result is slightly smaller (14.3) than the usual value of 15.5. It extends the range of usefulness of the ferrous sulfate dosimeter.

Taplin et al. (179) have given some more details on chlorinated hydrocarbons and aqueous pH indicator-dyes as chemical dosimeters more sensitive than ferrous sulfate. The aqueous phenol-red trichlorethylene is claimed to be useful either for long exposure periods or for small doses (0 to 300 r). Three dimensional examinations of two chemical systems irradiated in gel media were made by Gevantman et al. (180). The technique, which had already been proposed by Day & Stein (181) for methylene-blue, was tried again for combinations of agar and KI-starch and for trichlorethylene

bromocresol purple which changes from purple to yellow because of HCl production.

Physical studies related to dosimetry were carried out during the past year. Ranges of 6 to 18 Mev protons in Be, Al, Cu, Ag, and Au were measured by Bichsel *et al.* (182). Snyder & Neufeld (183) have examined the problem of the passage of heavy particles through tissue and calculated the variation of the linear energy transfer (LET) along the track of a proton, α-particle, carbon, nitrogen, and oxygen ions. A technique for tritium counting in glass proportional counting tubes was described (184). Calorimetric determinations of the beam power have been made in a 1400 kv. x-ray beam by McElhinney *et al.* (185). The results were compared with ionization chamber measurements. Assuming 33.9 for W in air, it can be calculated that the radiant energy per square centimeter equivalent to 1 r is 2985 ergs/cm.^{2} for 1400 kv. From experimental comparison between ionization current and calorimetry, the authors found 2983 ± 69 ergs/cm.^{2}/r. Calorimetric determination of the ratio of energy absorption, E_m, to measured ionization, J_m, was also developed by Skarsgard *et al.* (186) for 22 Mev x-rays. The authors have calculated a value of ρ_m, the stopping power ratio of carbon to air, since ionization measurements were effected in a graphite cavity-type chamber. From the usual Bragg-Gray relation $E_m = J_m W \rho_m$, the energy per ion pair in air, W, was deduced. The value of 32.8 was smaller than the generally assumed value of 34. The measured values of E_m/J_m for 22 Mev might also be used to estimate the conversion from roentgens to rads.

Several high intensity Co^{60} gamma sources were described. Russian workers of the Karpov Institute (187) gave characteristics on the design of shieldings and irradiation facilities for a 21,000 curies cobalt source which has been operating for several months. It provides a dose rate of 1200 r/sec. in a volume of 0.4 liter and 100 r/sec. for 100 liters. The source is introduced in the working chamber with the help of remote control mechanisms. Another type of design for large gamma irradiation units has been proposed by Murray *et al.* (188).

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ION EXCHANGE RESINS AND MEMBRANES[1]

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The phenomenon of ion exchange, recognized and studied in desultory fashion for many decades, became about twenty years ago the object of rapidly expanding interest and importance. The ensuing research has led to so many applications and related developments that ion exchange has become a unit process in the chemical industry as well as a standard tool in the research laboratory, and its study is common in many areas of physical and biological science. Thus one of the best general reviews of ion exchange appearing during the last year was a unit operations review [Kunin, Mc-Garvey & Farren (1)], and ion exchange techniques were routinely used in the concentration and separation of element 102, nobelium, the most recently announced new element and presumably the next to the last actinide [Milsted (2)]. The breadth of interest and application makes impossible a complete report of all the many hundreds of articles concerning one or another of the aspects of ion exchange which have appeared since the last *Annual Review* [Gregor (3)]. This review attempts to report illustrative investigations in a number of these areas with some emphasis on studies of the exchange systems, components, processes, and equilibria, and applications primarily of interest to the physical, inorganic, or analytical chemist.

The present state of the whole field of ion exchange and its applications was broadly surveyed in a number of review articles and books [Kitchener (4); Kahn, Lawson & Jones (5)]. Calmon and Kressman edited a new work in which a comprehensive discussion of general theory and practice, with a large bibliography, introduced chapters on specific applications in organic chemistry and biochemistry, including the separation of amino acids, peptides and carbohydrates, enzyme studies, sodium and potassium removal *in vivo*, applications in pharmaceutical and organic chemistry, catalytic applications, studies in plant physiology, and treatment of water and various natural products [Calmon & Kressman (6)]. Ion exchange technology was fully covered in both fundamental aspects and applications [Nachod & Schubert (7)]. Two works in general chromatography included topics in ion exchange; new material on gradient elution and ion exchange celluloses for protein chromatography was added to the brief historical and general discussion and the thorough bibliography in the second edition of a standard reference [Lederer & Lederer (8)]. A detailed presentation of the general theory and principles of chromatography was given in the second work which also includes extensive material on electron exchange polymers or

[1] The survey of literature pertaining to this review was concluded December, 1957.

[2] The reviewer is greatly indebted to David M. Mohilner for his assistance in the compilation of the literature references.

redox resins [Cassidy (9)]. An excellent short discussion of synthesis and general properties of ion exchange resins was belatedly published in a collection of twenty-one review papers on various aspects of the field [Society of Chemical Industry (10)]. A very extensive bibliography of almost two thousand references in two sections, applications and theoretical papers, accompanied a brief survey of resin structure and properties, performance data, ion exclusion, ion exchange membranes, and analytical and therapeutic applications [Osborn (11)]. The section on applications is divided by subject, but that on theoretical work contains papers on many different topics arranged only alphabetically by first author.

The general field of ion exchange was reviewed as one of the unit processes with a carefully selected bibliography and emphasis on theory, membranes, treatment of aqueous solutions, applications in the field of atomic energy, biochemical and medical separations, waste treatment, catalysis, apparatus and process applications, and recovery, purification, preparation and new resins [Kunin, McGarvey & Farren (1)]. A similarly comprehensive review of less technical but more fundamental aspects covered equilibrium and kinetics, exchangers in nonaqueous and mixed systems and in analytical chemistry, catalysis by ion exchange resins, the use of ion exchangers in determining the nature of complex ions, and the preparation of new and modified ion exchange resins [Magee (12)]. Other reviews covered some general topics in the field [Griessbach (13); Grefsgård (14)].

The various processes which may take place with ion exchange resins were summarized [Griessbach (15)]. Contemporary theories of ion exchange were used in a classification of exchangers [Nikol'skiǐ (16)]. The study of exchangers as highly disperse systems was investigated, with emphasis on the surface properties, pore structure and selectivity of the exchangers, the nature of permselective membranes, and the deionization, fractionation and flocculation interactions between ion exchangers and colloid systems [Griessbach & Richter (17)]. All three of these reviews contain material of general usefulness.

Methods of calculation and the interpretation of experimental results were summarized [Gladel (18)]. Ion exchange separations were reviewed with particular reference to selectivity coefficients for the exchanges of pairs of ions, absorption coefficients for mixed solvents, and solvent uptake [Bonner (19)].

Mineral Exchangers

The study of ion exchange originated in investigations of the behavior of clay minerals, and interest has not abated in these systems. Barrer continued his studies of aluminosilicates and investigated inclusion complexes of hydrocarbons with faujasite and sorption and intercalation in methyl ammonium montmorillonites [Barrer et al. (20)]. The adsorption of azotized organic molecules on montmorillonite was reported to occur by simultaneous base exchange and interlamellar adsorption [Haxaire & Bloch (21)]. The effect of

exchange cation and anion on the adsorption of hydrolyzed polyacrylonitrile on kaolinite was studied [Mortinsen (22)]. The location and orientation of organic molecules or radicals in clay structures is of interest and it was suggested that in complexes of simple alcohols with montmorillonite the plane of the carbon chain is perpendicular to the (001) plane [Emerson (23)]. Organic derivatives of clay minerals are not generally stable to chemical treatment; when phenylmontmorillonite was treated repeatedly with strong alkali and then strong acid, the material was extensively degraded, although many Ph—Si bonds were retained in the fragments of low molecular weight extracted by toluene [Gentili & Deuel (24); Deuel (25)]. The toluene extract contained cyclotrisiloxanes, cyclotetrasiloxanes and acylic siloxanes, but few compounds with Si—OH bonds.

Cation exchange in soil materials was investigated for K [Blanchet (26)] and Cu and Zn [DeMumbrum & Jackson (27)]. The exchange of Au with Na and Ca in clays was found to be quite appreciable when one phase is solid, but extremely slight when both phases are solid. The results were related to natural processes in which soils delivered nutrients or metal ions to plants at a much lower moisture level than exists in clay pastes or suspensions [Chatterjee (28)]. Loosely and firmly bound states of a given cation in clays were demonstrated by exchange experiments between NH_4-Ba clays or NH_4-Na clays and H resins in cellophane bags [Chatterjee (29)]. The exchange of phosphates adsorbed on clays for other anions was described [Chatterjee (30)]. Cationic reactions at the surface were investigated for feldspar [Nash & Marshall (31)] and mica [Gaines (32)]. Ion exchange of Cs, Ba and H occurred rapidly with surface K ions but no penetration of other cleavage planes was observed with neutral salt solutions. The exchange capacity, 3.48μeq./sq.m., could be calculated from the crystal lattice parameters.

The adsorption of phosphate on various cation forms of montmorillonite was found to decrease in the order $Ca > Al > Be > Ba > Mg > H > Hg > NH_4 > K > Na$ [Mitra Prakash (33)]; the nature of the adsorption and mechanism of the surface reaction were discussed. The adsorption of water on kaolinite was determined at 15.6°, 25.0° and 35.0°C., and the heats and entropies of adsorption calculated. Adsorption on Li, Na and Ba clays was also measured at 25.0° [Goates & Bennett (34)]. Hydration and hydroxylation problems were reviewed with particular reference to montmorillonite [Mackenzie (35)].

The diffusion rates of NaI and urea were determined in montmorillonite and kaolinite pastes, and radioactive isotope measurements were used to determine the self-diffusion rate of Na and I ion [Blocksma (36)]. The mobility of I ion was only 40 to 50 per cent of its value in aqueous solutions, and that of Na ion was an even smaller fraction of the value in aqueous solution. Diffusion apparently occurs via a complex path in a porous medium. The electrochemical properties of bentonite suspensions were investigated [van Olphen (37); Uskov & Uskova (38)]. Thixotropy, mechanical properties, swelling and exchange properies were studied for montmorillonite [Hofman,

Fahn & Weiss (39)] and askangel [Kobakhidze, Shishniashvili & Serbina (40)]. Hydronium forms of the aluminosilicates, analcite and chabazite, were prepared by treatment of the Ag forms with aqueous solutions of pyridinium chloride; the pyridinium ion is too large to enter the crystal, and AgCl precipitates [Beattie & Dyer (41)].

Treatment of soil materials with either $Ca(OH)_2$ and a vinyl acetate-maleic acid copolymer, hydrolyzed polyacrylonitrile, or the copolymer of isobutylene and the half NH_4 salt—half amide of maleic acid (soil conditioners) increased the cation exchange capacity from 2 to 12 per cent [Allison (42)]. It was suggested that the polymer is adsorbed forming bridges in the clay structure and that intermediate groups on the polymer chain participate in the exchange process.

The adsorptive and catalytic power of active or activated carbon has been interpreted in part in terms of phenolic, lactone and chromene structures. The ion and electron exchange properties of activated carbon were summarized from this point of view [Garten & Weiss (43)]. Hydrous ZrO_2 was reported to act as an amphoteric monofunctional exchanger, the capacity for either anions or cations varying regularly with pH [Amphlett, McDonald & Redman (44)]. Such inorganic exchangers may be useful substitutes for organic resins at high temperatures or radiation levels.

PREPARATION AND PROPERTIES OF RESINS

A very extensive survey of methods of resin synthesis was included in the last *Annual Review* [Gregor (3)]. Of the many new or modified resins and methods of preparation only a few more or less illustrative examples will be given here. The preparation of mechanically strong, hard, strong acid cation exchange resins by the sulfonation of acenaphthene with fuming H_2SO_4 followed by condensation with formaldehyde was reported [Petrov & Titov (45)]. Cation exchange resins of the carboxylic type of high exchange capacity and high resistance to chemical attack were prepared by saponification of the homogeneous resin resulting from the polymerization of acrylonitrile and a divinyl compound with a dispersing agent ["Montecatini" Società Generale per L'Industria Mineraria e Chimica (46)]. A polyether cross-linking agent was used in the synthesis of carboxylic polymers by the copolymerization of acrylic and maleic acids or anhydrides with a polyalkenyl polyether of a polyhydric alcohol [Brown (47)]. The product from acrylic acid and a polyallyl polyether of sucrose exhibited a cation exchange capacity of 11 m.eq./gm. and high swelling properties. Cellulose ion exchange resins containing 0.35 to 0.5 m.eq. of sulfonate groups per gram were prepared from $ClCH_2SO_3Na$ and cellulose powder in NaOH [Porath (48)]. Sulfoethyl cellulose was similarly synthesized; triethylaminoethyl cellulose was prepared in the Br form from diethylaminoethyl cellulose and C_2H_5Br. These cellulose exchangers are useful in fractionations of natural substances, e.g. posterior pituitary hormones or folic acid and its derivatives. Cation exchange resins were prepared from cashew nut shell liquid [Krishnaswamy,

Govindan, & Pandya (49)], comminuted shale tar coke [Kozhevnikov (50)], and carbon [Brinkman & Niemann (51)].

Trihydroxymethylphenol was condensed with a phenol and an alkylene polyamine or polyethyleneimine to produce anion exchange resins of high mechanical stability [Farbenfabriken Bayer A.-G. (52)]. Anion exchange resins cross-linked with polyesters of unsaturated polycarboxylic acids were described [D'Alelio (53)]. Anion exchangers particularly suitable for extraction of silicate and carbonate were prepared from aminoalkyl or quaternary ammonium alkyl derivatives of halogenated copolymers of monovinyl aryl compounds and polyvinylaryl cross-linking compounds [Gilwood & Greer (54)]. Sulfonated cation exchange resins treated with excess NH_4OH or an amine at high temperature and pressure were reported to yield anion exchangers [Davankov & Vekhets (55)]. Anion exchange polymers were synthesized from sodium cellulose xanthate and polyethyleneimine [Sonnerskog (56)], and from methyl vinyl ketone [Suda, Inoue & Oda (57)]. Both strongly basic and weakly basic anion exchanging fibers were described [Motozato, Egawa, Nagata & Nakanishi (58)]. Improvements were reported in the synthesis of quaternary ammonium anion exchange resins from halomethylated vinyl aromatic compounds [Clarke & Hamerschlag (59)].

Ion exchange resins were described containing boric acid groups [Solms & Deuel (60)] and phosphate groups [Kennedy (61)]. The Na-diallyl-phosphate polymer had an acid exchange capacity of 4.4 m.eq./gm.; the acid form at pH 1.0 sorbs cations in the order $Th^{4+} \gg Fe^{4+} > U^{6+} > La^{3+} > Ba^{++} > Na^+$; and U^{6+} may be eluted with aqueous $(NH_4)_2CO_3$. A sulfonated phenol-formaldehyde resin in which chromotropic acid had been incorporated was reported to be selective for Ti [Klyachko (62)].

An amphoteric exchanger was prepared having organic acid and basic N groups attached to the same resin matrix; its capacity was 2.5 m.eq./gm. for anions and 3.0 m.eq./gm. for cations [Hale, Thomas & Pepper (63)]. Polyampholytes from hydroxylamine and polyacrylonitrile in dimethyl-formamide were reported to contain free amidoxine groups and no glutaro-imidedioxime rings [Schouteden (64)].

Sulfonation and sulfation were reviewed with reference to ion and electron exchangers [Gilbert & Jones (65)]. A novel method was suggested for the preparation of highly permeable polymers, involving the incorporation of silica gel particles and their subsequent removal with HF solution [Wagner (66)]. Graft copolymers produced by γ-irradiation were sulfonated to give resins of high mechanical strength, permselectivity, and conductivity [Chen et al. (67)].

The preparation and properties of naphthaquinone, anthraquinone, and hydrophilic mixed condensation redox resins were described [Manecke & Bahr (68)]. Syntheses were reported for polymers of 2,5- and 3,5-dihydroxy-phenylalanine [Harwood & Cassidy (69)] and of bis-methoxymethyl ethers of dihydric phenols [Stern, English & Cassidy (70)]. Electron exchangers were reviewed [Cassidy (9)].

The swelling and cation exchange properties were described for phenol-formaldehyde resins containing monophenyl and monohydroxyphenyl phosphates, hydroxybenzenearsonic acids, and monobenzene- and di-hydroxybenzenesulfonic acids [Trostyanskaya, Losev & Tevlina (71)]. The structure, swelling, and mechanical and optical properties of a phenosulfonic acid-formaldehyde resin were investigated [Koschel & Schlögl (72)]. The cross-linking and scission processes which occur in resins exposed to high energy radiation were discussed in terms of free radical mechanisms and double bond formation [Simha & Wall (73); Okamoto & Ishihara (74)]. The degradation of cross-linked resins caused by heating under pressure or heating with H_2O_2 and Fe or Cu catalyst was described [Wood (75)], and the relationship between degradation and swelling, particle size, stability and concentration of cross-linking agents, and resin structure was discussed [Collins, Litterio & Markus (76)]. In regular use quaternary anion exchangers lose capacity because of peroxy radical attack on amine structure or because of adsorption of complex natural organic acids [Frisch & Kunin (77)]; exchangers generally decrease in effectiveness also because of powdering due to swelling processes [Meleshko, Chervinskaya, Romanov & Izmaĭlova (78)].

Interesting studies were described of the dependence of dry gas and water absorption by cation exchangers on the nature of fixed anion and exchangeable cation present [Sarin & Puri (79)], and of the behavior of ion exchangers loaded with soaps [Richter (80)]. Cation exchangers sorb soap cations very tightly and the occluded anions are exchangeable; with anion exchangers more involved phenomena result from association of soap within the resin skeleton.

Theory, Kinetics, and Equilibrium

The selectivity of ion exchange resins and its dependence on cross-linking, exchange capacity, and solution composition were treated in terms of the theory of binding of ions to polyelectrolytes [Harris & Rice (81)]. The molecular model for linear and cross-linked polyelectrolytes and intrinsic ion pairing constants lead, through the use of the methods of cell theories of liquids for the electrostatic free energy and that of Flory for the configurational free energy of an uncharged gel, to predicted selectivity quotients which vary with solution composition in the experimentally observed manner.

The mechanism of sorption of dipolar ions by exchangers was discussed [Samsonov & Kuznetsova (82)], and the principle and elementary theory of "focusing ion exchange" were described with application to rapid separations and analyses [Schumacher (83)].

The theory of the movement of the steady front was developed for the dynamic sorption of univalent ions and satisfactorily tested with Rb-NH₄ exchange studies [Rachinskiĭ (84)]. Other earlier work on sorption dynamics was extended to the variation of the sequence of moving components with changing solution concentration [Samsonov & Orestova (85)]. Band structure in chromatography was derived on the assumptions of one-site and two-site

processes and linear adsorption properties [Giddings (86)]. Asymptotic equations for ion exchange filtration were developed from an assumed simple distribution relation and rate expressions, and verified by measurements of Na-H exchange [Anokhin (87)]. A simplified interpretation of kinetic data in ion exchange columns was presented in terms of linear equilibrium [Bucay (88)].

In the case of film diffusion controlled exchange of ions of different mobilities, ion diffusion produces an electric potential gradient which may influence markedly the rate. A detailed analysis of the effect showed that if the exchanging cation possesses a diffusion constant smaller than that of the cation in the resin, then the initial flux of exchanging ion is larger, the exchange half-time smaller, and the subsequent flux smaller than the corresponding values calculated without consideration of the field. The effects are more pronounced for higher valent cations [Schlögl & Helfferich (89)].

A method was described for the study of exchange rate and concentration gradient by interferometric observation of color fringes in white polarized light passed near a grain of exchanging resin [Follenius & Platzer (90)].

The heats, free energies and entropies of exchange were reported for various pairs of ions on a cross-linked polystyrene-sulfonate resin, and compared with corresponding quantities for exchange between aqueous chloride solutions of the same concentrations and pressures as in the resin [Cruickshank & Meares (91)]. The theoretical bases and practical methods of determining exchange equilibrium constants were described [Jangg (92)], and exchange constants for H-Na exchange on Permutit RS were presented. The apparent constant decreases with rising temperature and increasing solution concentration. Exchange equilibrium was studied for Na-Zn, Na-Cu, and Na-Mn on a sulfonated phenolic resin in nitrate and polymetaphosphate solutions [Djurfeldt & Samuelson (93)]. Exchange studies on Dowex 50 resin were reported for Fe(III)-H [Vasishth & David (94)], Cu-Na [Subba Rao & David (95)], and Zn-H [Meyer, Argersinger & Davidson (96)]. A selectivity scale for common uni- and divalent ions on Dowex 50-X4, 8, and 16 was described based on the value unity for Li (Bonner & Smith (97)]. The order of increasing preference is the order of decreasing mean activity coefficients of the nitrates in aqueous solution.

Exchange in concentrated solutions was investigated with Mg, Na, K, Cl, and SO_4 [Kassner (98)], and in the ternary systems Na-Ag-H, and Cu-Ag-H [Dranoff & Lapidus (99)]. Equilibrium between pairs in the ternary system could be calculated from data for the separate binary systems.

The sorbability of tripositive lanthanides on the H form of Dowex 50 from dilute $HClO_4$ at 25°C. was found to decrease from La to Dy and then remain constant for the heavier elements; Am and Cm were sorbed like the lanthanides of equal crystallographic radius. The heats and entropies of sorption were determined for Pm, Tm, Lu, and Am [Surls & Choppin (100)]. A radiochemical study of the sorption and exchange of Sr^{2+} and Ce^{3+} on a sulfonic exchanger was reported. The chromatographic process occurs under

nearly equilibrium conditions for a wide range of resin composition [Elovich & Prusakov (101)].

Gradient elution has become extremely useful in many separations. The theory of gradient elution through ion exchange resins was described and extended to treat a variable number of effective plates [Schwab, Rieman & Vaughan (102); Freiling (103)]. Peak locations and shapes and the elution history curve were predicted from theory and verified by experiment. A typical application of both continuous and discontinuous gradient elution was reported in the separation of deoxypolynucleotides released in mouse spleen by x-irradiation [Main, Cole & Ellis (104)]; sodium phosphate buffer eluant was used on a calcium phosphate column. A gradient elution effect was noted when the temperature fell from 93°C. to 33°C. during elution of Sc, Lu, Yb, Tm, Er, and Ho from Dowex 50 with NH_4 α-hydroxyisobutyrate [Stewart (105)].

Membranes

Ion exchange membranes are of interest in the fundamental study of exchange systems, transport phenomena, and biological problems, and have practical usefulness in separations, concentrations, and electrochemical studies. For such purposes reproducible, mechanically strong, highly selective membranes are needed. Homogeneous membranes were prepared by evaporation of solvent from solutions containing a polyelectrolyte (polystyrenesulfonic acid, a polycarboxylic acid, or a quaternary ammonium polyelectrolyte) and a film-forming polymer such as Dynel [Gregor et al. (106)]. Such membranes are highly ion-selective, the measurement of concentration potential indicating only small "leaks" of the ion of opposite charge. The films are nearly impermeable to nonelectrolytes like sucrose, and in some cases are highly ion specific. Anion permselective membranes having good mechanical and electrical properties and exchange capacity >0.3 m.eq./gm. were reported from the haloalkylation of a screen of aromatic vinyl polymer following by treatment with a tertiary aliphatic amine [Clarke (107)]. Films of water soluble anionic polyelectrolytes containing epoxy groups and water dispersible polymeric nonelectrolytes were heated to give stable, water permeable, insoluble membranes with cation exchange properties [Jackson (108)]. Membranes of low water permeability and exchange capacity but very high anion selectivity were prepared by soaking preformed porous collodion matrices in aqueous solutions of poly-2-vinyl-N-methylpyridinium bromide [Gottlieb, Neihof & Sollner (109)]. The preparation of resin membranes and their use in extraction, sorption and electrodialysis were described [Trostyanskaya, Losev & Tevlina (110)]. The method was reported to allow wide variation of permeability, capacity, and elasticity. Specific membranes of cellophane impregnated with $BaSO_4$ were described [Hirsch-Ayalon (111)], and membranes of low melting paraffin containing a slightly soluble Ca salt and a nonionic detergent were reported to be specific to Ca ion [Tendeloo & Krips (112)].

Multilayer membrane electrodes of Ba stearate were reported to be

specific to Ba^{++} transport [Gregor & Schonhorn (113)]. A lipoidal membrane system was described prepared from oleic acid and aqueous KCl containing egg albumin; the system showed differential permeability to cations [Monnier & Monnier (114)].

Very many experimental studies were reported for membrane systems. The influence of stirring, flow rate, concentration gradient, membrane swelling, and ion or molecule size on the separation of electrolytes and simple nonelectrolytes by means of ion exchange membranes was investigated; electrolyte permeability, osmotic pressure, and the simultaneous diffusion of NaCl and $MgCl_2$ were measured [Manecke & Heller (115)]. In a cell with a strong acid cation selective membrane, a strong base anion selective membrane, and with NaCl as electrolyte, the maximum current density was limited by hydrodynamic flow conditions; the effect on diffusion rates agreed with theory at the anion membrane but was significantly higher at the cation membrane. Variations of pH, concentration, flow rate, and geometry were studied [Rosenberg & Tirrell (116)]. Relative transport numbers and selectivity coefficients of K, Na, Mg, and Ca and electro-osmotic water transport were measured for a phenosulfonic acid resin membrane. Na permeates the membrane more extensively than Mg and Ca and less than K; for two ions the ratio of transport numbers is nearer unity than the product of selectivity and mobility ratios [Oda et al. (117)]. Similar membrane studies were reported for NaCl solutions at high concentrations [Madgwick (118)]. The preparation and electrochemical behavior of a double ion exchange membrane were described (Oda, Murakoshi & Saito (119)]. Concentrations in the membrane, interdiffusion, self diffusion, exchange isotherms, conductance and bi-ionic potentials were measured in Na-H, Na-K, and Na-Sr bi-ionic membrane systems [Helfferich & Ocker (120)]. Studies of single ion concentration potentials and multiple ionic potentials were reported [Chaussidon (121)].

Electro-osmotic water transport in cation membranes was correlated with exchange capacity and shown to be primarily responsible for small deviations of concentration potentials from ideal behavior; large deviations were ascribed to degradation of the membrane by Cl ion diffusion [Stewart & Graydon (122)]. The relative water mobility and Hittorf cation transference numbers were determined for a cation membrane [Oda & Yawataya (123)]. An isotopic tracer method for high precision measurements of water and ion transport was described [McKelvey, Spiegler & Wyllie (124)].

Normal and anomalous osmosis were investigated for oxyhemoglobin membranes (positively charged at pH 4.0 , uncharged at pH 6.75, negatively charged at pH 10.0) with a variety of electrolyte solutions over a wide concentration range [Grim & Sollner (125)]. In phenol-acetic acid-water solvent the cations of many polypeptides and simpler proteins were found to have similar mobilities in denitrated collodion membranes [Synge (126)].

Three interesting membrane phenomena were demonstrated. When solutions of ionic surface active agents are dialyzed through cellulose, the membrane adsorbs the agent and becomes permselective to the counter ion

[Kushner & Parker (127)]. In the exchange of ions through selective membranes the system overshoots the final equilibrium state if the exchange rates are greatly different. This may be related to the accumulation of ions against concentration gradients in living cells [Neihof & Sollner (128)]. Gravitational convection in enriched or depleted electrolyte solutions near membranes in a horizontal membrane cell gives rise to vertical concentration gradients and, if the mobilities are different, to electrogravitational fractionation of ions [Frilette (129)].

The use of ion exchange membranes in concentrating electrolyte solutions was shown in detailed experiments with NaCl; the results were in accord with the previously developed theory [Ishibashi, Seiyama & Sakai (130)]. Many proposed applications and devices were described, including a desalting cell with alternate cation and anion membranes and a redox ion solution circulating between the electrode chambers [Roberts (131)].

The general theory of Donnan membrane equilibrium was extended to include ions of finite size and local activity coefficients [Hill (132)]. Simple membrane models were used to obtain theoretical relations among the measurable inward and outward fluxes, internal and external ionic concentrations, and potential difference across the membrane [Harris (133); Kobatake (134)]. A detailed theoretical analysis of membrane-solution equilibrium and transport was published [Patlak (135)].

POLYELECTROLYTES

Polyelectrolytes represent the limiting case of ion exchangers of vanishingly low cross-linking [Harris & Rice (81)]. Studies of polyelectrolyte properties and behavior, then, may be related to ion exchange studies: ion binding in polyelectrolytes, for example, to ion specificity in exchangers. The binding of counter ions to spherical polyelectrolytes was treated in terms of the electrostatic effects in two models; in either case the extent of binding was found to increase with increasing polymer size so that ion exchangers, of essentially infinite size, exhibit maximum binding capacity [Wall (136)]. The binding of H ions to plasma albumin was discussed in terms of cooperative transitions [Foster & Aoki (137)], the binding of Cl ions to serum albumin on a hydrogen bonded model [Saroff (138)], and the binding of K and Na ions to muscle proteins on a hydrogen bonded and chelated model [Saroff (139)]. The equilibrium between free counter ions and ions associated with fixed polyelectrolyte groups was treated in its relation to potentiometric titration curves [Lifson (140)] and to osmotic and activity coefficients in polyelectrolyte solutions and swelling force in gels [Osawa (141)]. It was pointed out that configurational and electrostatic contributions are not strictly additive, in either free energies or potentials, in theoretical treatments of polyelectrolytes [Lifson (142)], and that diffusion measurements in gel-solution systems may have restricted validity because of the different degrees of heterogeneity in the several parts of the system [Crouzat-Reynes (143)].

Characteristic data were summarized for a number of polyelectrolyte cations, anions and amphoteric ions [Thiele & Langmaack (144)]. The binding of counter ions to polyelectrolytes was investigated with the use of ion exchange membranes as electrodes reversible to small ions in anion-serum albumin systems [Scatchard, Coleman & Shen (145)], by electrophoresis, solubility, and viscosity studies in cation-polyphosphate systems [Strauss, Woodside & Wineman (146)], and by electrical transference and diffusion methods in systems containing Sr ion and polyacrylic acid or styrene-maleic acid copolymer [Wall & Eitel (147)]. With the polyphosphates the data indicated site-binding with Li, Na, and K but not with tetramethylammonium ion. Viscometric and conductometric titrations of polymethacrylic acid and potentiometric titrations of polyacrylic and polymethacrylic acids, with Li, Na, K, NH_4, tetramethyl-, ethyl-, propyl- and butylammonium hydroxides showed Li, and to a lesser extent Na, bound to the polyacid. With increasing cation size the slope of the titration curve and the average ionization constant of the polyacid increased, suggesting that even the large ions are close to the polyanion chain. The results were in agreement with dissociation theory extended to include counter ion size [Gregor *et al.* (148)]. The dependence of the degree of ionization of swollen cross-linked polyelectrolyte gels on pH was investigated by potentiometric titration, and ideal Donnan and electrostatic interaction terms were included in the discussion [Michaeli & Katchalsky (149)]. The neutralization curves of a resorcinol-formaldehyde resin (two weak acid groups) and Amberlite IR100 (a strong acid and a weak acid group) were analyzed [Gupta (150)]. Activity coefficients of counter ions were determined electrometrically in solutions of K polystyrenesulfonate [Cerny (151)], of Na polystyrenesulfonate, carboxymethylcellulose, polyvinyl alcohol sulfate, and cellulose sulfate [Nagasawa & Kagawa (152)], and of Ag salts of polyacrylic acid, carboxylmethylcellulose, and copolymers of acrylamide and either acrylic or maleic acid [Dobry-Duclaux (153); Bourdais & Dobry-Duclaux (154)]. The different investigators were not in accord on the qualitative variation of activity coefficient with dilution; the coefficient was reported to be independent of degree of polymerization but a function of the density of ionizable groups on the polyelectrolyte, and the latter relationship was extended to predict that for strongly adsorbed ions, the selectivity of an ion exchanger increases with increasing density of exchange loci. The reduced osmotic pressure of a polyelectrolyte solution containing added biunivalent salts was observed to be linear in the polymer concentration as is true with added NaCl. The osmotic coefficient involves ion-polyelectrolyte association [Inagaki, Hotta & Hirami (155)].

The conductivity of solutions of K salts of carboxymethylcellulose and sulfonated polystyrene with added KCl was observed to decrease with increasing polymer content at constant small ion concentration; the discrepancy with theory was dicussed in terms of relaxation effects [Longworth & Hermans (156)].

The fractionation of polyelectrolytes on ion exchangers was shown to de-

pend on the porosity but not the degree of cross-linking in the resins [Hartler (157)]. The dependence of size and shape of chain-like polyelectrolyte molecules on the nature of exchangeable ions was investigated [Cooper & Wassermann (158)]. Membranes of graded porosity were produced by the controlled hydrolysis of homogeneous polyvinylbutyral films in $4N$ H_2SO_4 at 60°C. [Gregor & Kantner (159)] and by swelling of collodion membranes in ethanol solutions of graded concentrations [Carr, Anderson & Miller (160)].

Anisotropic gels produced from interdiffusing polyelectrolyte solutions were described as resembling both ion exchangers and natural globulins or other proteins, and these synthetic gels were compared with native biological structures such as actin and myosin [Thiele & Langmaack (161)].

INORGANIC STUDIES AND COMPLEXES

A discussion of the ion exchange behavior of the transuranium elements was published [Graf (162)]. The separation of nobelium was accomplished on a cation exchange column by elution with α-hydroxybutyric acid; it was distinguished from Th^{225} by elution with 6 N HCl, which removes actinides but leaves Th [Milsted (2)].

Ion exchange is a valuable tool in determining the nature of ionic species in solution [Ray & Ray (163)]. The anion exchange behavior of quadrivalent actinides was reported [Saito & Sekine (164)]. Exchange rate and equilibrium studies in UO_2SO_4 solutions suggested the presence of $U_2O_5(SO_4)_2^{-}$ in concentrated solutions and in dilute solutions a transition from $UO_2(SO_4)_3^{4-}$ to $U_2O_5(SO_4)_3^{4-}$ with increasing pH [Arden & Rowley (165)]. Th was found to exist as $ThCl_2^{++}$ at all pH values in various chloride solutions, as $Th(NO_3)_2^{++}$ generally in nitrate solutions, and as $Th(HSO_4)^{+++}$ in sulfate solutions [Schulz & Herak (166)]. Po was reported to form $Po(OH)Cl_4^{-}$, $PoCl_6^{-}$, $PoO(NO_3)_3^{-}$ and $Po(NO_3)_5^{-}$ anions, the nitrate species being in equilibrium with appreciable concentrations of positively charged ions even in 5 N HNO_3. The ion exchange data were used to discuss redox behavior of Po as well [Danon & Zamith (167)]. A new method was used to establish the formulas of Ru^{+++} and $RuCl^{++}$ in aqueous solution [Cady & Connick (168)].

In other exchange studies Ge was shown to exist primarily as $Ge(OH)_xCl_{5-x}^{-}$ or $Ge(OH)_xCl_{6-x}^{-}$, $3 < x < 4$, in 6 to 9 N HCl. These complexes are converted to the dioxide at lower acid concentrations and to the tetrachloride at higher concentrations [Everest & Harrison (169)]. The principal species of Sn(IV) in HCl are $SnCl_5^{-}$ and $SnCl_6^{-}$, and perhaps chlorostannate at low HCl concentration [Everest & Harrison (170)]. Aqueous solutions of H_3AsO_3 contain $As_3O_5^{-}$ changing to $As_2O_4^{-}$ from pH 5 to 9, and to $H_2AsO_3^{-}$ between pH 10 and 11, and mainly $HAsO_3^{=}$ above pH 11; $AsO_3 \equiv$ may exist at pH greater than 12.5 in low As concentrations [Everest & Popiel (171)]. Be exists in high F ion concentration as BeF_4^{-}, not BeF_3^{-} [Ray (172)]. The adsorption behavior of Yt on SO_4 or CO_3 anion exchanger was reported [Saito & Sekine (173)]. Other studies concerned the exchange of silicic acid [Davydov & Davydova (174)] and borate ions [Yamabe (175)],

and the adsorption of bromine and iodine [Aveston & Everest (176)]. Anion exchange was used in part to demonstrate that so-called "triphenylchromium" is probably benzenebiphenylchromium [Hein, Kleinert & Kurras (177)].

Cation exchange resins in the H form were used to prepare free acids from $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ [Basiński, Sierocka & Schmidt (178)] and various polyphosphates [Klement & Schmid (179)].

The principles of the use of ion exchange in the study of complexes were summarized [Paramonova (180)] and a good review of chelating and complexing resins was published [Millar (181)]. The formation constants of twenty Mn(II), four Co and three uranyl complexes with organic acids were reported. The assumption that the complex is not taken up by the resin was confirmed [Li *et al.* (182)]. Zn and Cd were shown to form 1:2 complexes with oxalate and tartrate, Zn a 1:2 complex with thiosulfate, and a 1:1 complex with citrate. The instability constants were listed [Korshunov, Pochinaĭlo & Tikhomirova (183)]. Ag forms predominantly a 1:3 complex with thiosulfate [Marcus (184)]. With ethylenediaminetetraacetic acid, Pu(III) and Pu(IV) form 2:1 and 1:1 complexes and Pu(VI) a 1:1 complex; the pK's for the 1:1 complexes are 18.12, 17.66, and 16.39, respectively [Foreman & Smith (185)].

Lanthanides were eluted from Dowex 50 by NH_4SCN solution in decreasing atomic number sequence, and actinides were eluted before lanthanides of corresponding size because of their stronger thiocyanate complexing. On Dowex 1 the sequence varied with temperature and eluant concentration (Surls & Choppin (186)]. Exchange studies indicated the existence of polynuclear phosphato-ferric and phosphato-sulfato-ferric ions in $Fe_2(SO_4)_3$ —H_3PO_4—H_2SO_4 systems [Holroyd & Salmon (187)].

Cu(II) was reported to form complexes with acrylated amino acids, the stability of which is markedly decreased by acetylation of the nitrogen of the ligand [Weiss & Fallab (188)]. Monogermanic acid was found to form no complex with ethylene glycol, none with glycerol at pH <9, a 1:1 complex with glycerol at pH >9, and 1:1 and 1:2 complexes with mannitol [Everest & Harrison (189)].

The behavior and uses of ion exchange resins in nonaqueous solvents were described [Renault (190); Bonner (19)]. Basic functional groups in exchangers were titrated with perchloric acid in glacial acetic acid with Crystal violet or Oracet Blue B indicator [Ficken & Lane (191)].

Separations and Analytical Applications

A few more or less typical examples of the hundreds of reported separations will be mentioned here. Tetra-, penta-, hexa-, hepta- and octaphosphates were isolated on Dowex 1 with eluant of 0.005 N Na maleate and 0.18–0.30 N NaCl [Busch, Ebel & Blanck (192)]. Fe(III) was separated from Ni, Ca, Cu, Zn, Pb, Sr, Mg, Ca, Ba, and Al by adsorption on carboxycellulose at pH 2, the other ions being eluted with 0.01 N HCl [Ivanov, Lenshina & Ivanova (193)]. Spectroscopically pure Hf and Zr oxides were

prepared by differential elution of a mixture on an anion exchanger [Rajan & Gupta (194)]. The six alkaline earth ions were separated by elution from a resin column with ammonium lactate [Milton & Grummitt (195)]. Gram quantities of Am were separated from a kilogram of La by ammonium citrate elution from Dowex 50; the 15 curies of α-activity caused no adverse effects [Armstrong *et al.* (196)]. The separations of U from heavy and medium weight metals and of Te, Ru, Cs and the lanthanides from one another were reported in sulfate solution on Dowex 1 [Šušič (197)].

Lanthanides have been separated on resin columns by elution with citrate, lactate, thiocyanate, α-hydroxyisobutyrate, and hydrochloric acid, among others. New separations were reported with ethylenediaminetetraacetic acid [Brunisholz (198); Marsh (199)], β-oxyethyliminodiacetic acid [Wolf & Massone (200)], and the Zn complex of ethylenediaminetetraacetic acid on Zn resin [Fuger (201)].

The use of ion exchangers in separation of organic acids was described and compared with other techniques [Asselineau (202)]. Nine alcohols were separated on an ion exchange column by elution with graded $(NH_4)_2SO_4$ solutions; it was suggested that the alcohols replace water molecules at the exchange sites in the resin [Sargent & Rieman (203)]. The partition of ethanol and water and of glucose in ethanol-water mixtures was described [Rückert & Samuelson (204)]. Xylose, arabinose, galactose, and rhamnose were isolated from sulfite liquor [Shaw & Dignam (205)]. The separation of *cis*- and *trans*-isomers was reported for 4-chloro- and 2,4-dichlorocinnamic acid [Lindenfors (206)] and for dithiocyanatotetraquochromium (III) ion [Hougen, Schug & King (207)]. Tartaric acid was resolved by the preferential transfer of the D form through a membrane of 2-(D-gluco-D-gulo-heptahexahydroxyhexyl) benzimidazole in collodion or cellophane [Klingmüller & Gedenk (208)].

A rapid anion exchange method was described for the separation of organic from inorganic iodine [Blanquet *et al.* (209)]. The phenomenon of ion exclusion was investigated in detail for the system glycerol-water-NaCl-Dowex 50 [Bucay & Cory (210); Shurts & White (211)]. Common amino acids were freed of salt by displacing them from a cation exchanger with piperidine [Buchanan (212)].

Fifty-nine different peptides were isolated and identified by ion exchange chromatography of partially acidic hydrolysates of white turkey feather calamus [Schroeder *et al.* (213)]. Ion exchange separations were reported for adenosine mono-, di-, tri-, and tetraphosphates [Liebecq, Hunebelle & Louis (214)], and for serine, threonine, phosphoserine, and phosphothreonine [Schormüller, Belitz & Lehmann (215)]. Tobacco mosaic virus was fractionated with citric acid-Na_2HPO_4-NaCl eluant on a cellulose exchanger [Cochran, Chidester & Stocks (216)].

Ion exchange separations were tabulated in good detail with many references in a review of their use in analytical chemistry [Schindewolf (217)]. The analytical use of anion exchangers was described in separations of chloride complexes of a number of metals [Liška & Klir (218)], and analyti-

cal applications were discussed with particular reference to elution by the chelating agents ethylenediaminetetraacetic acid or 1,2-cyclohexanediamine-tetraacetic acid [Wünsch (219)]. Earlier studies of the use of ion exchange resins to increase the sensitivity of spot tests or precipitation reactions in microanalysis were extended to procedures for Bi, Cu, Ni, Co, and Fe [Fujimoto (220)]. Malic acid was separated from lactic, glycolic, and glyceric acids by $(NH_4)_2CO_3$ elution on a carbonate anion resin; malic acid is retained with dilute eluant [Goodban & Stark (221)]. An interesting procedure was reported for the determination of oxygen in water with the use of ion exchange resin loaded with $Mn(OH)_2$ or $Fe(OH)_2$; the spent resin can be regenerated by treatment with H_2SO_3 [Potter & Whitehead (222)].

An extensive review of paper chromatography and paper electrophoresis was published [Grüne (223)]. It includes details of many analytical methods.

CATALYSIS AND OTHER TOPICS

Ion exchange resins have been used as catalysts in a number of reactions such as hydrolysis, condensation, esterification, inversion, and dehydration. The exchanger-catalyzed condensation of mesityl oxide and trioxymethylene was reported [Wiemann & Thuan (224)]. A series of papers described the catalytic preparation of acetals from alcohols and ethyl vinyl ether and of cinnamic aldehydes from acetals and benzaldehyde; the Mannich, Kno-evenagel and cyanoethylation reactions with exchanger catalysts were described [Mastagli *et al.* (225)]. The selective amide hydrolysis of 1-benzoyl-1,2-dihydroquinaldamide was accomplished with an ion exchange resin catalyst [Collins (226)]. Detailed kinetic studies were made of the exchanger-catalyzed isomerization of D-glucose [Thompson (227)], decomposition of diazoacetic ester [Noller and Hässler (228)], and hydrolysis of dextrin [Anand & Puri (229)]. Porosity was more important than exchange capacity, and a diffusion effect was proved for fast reactions in aqueous solution.

The molecular sorption and desorption of phenol on ion exchange resins was investigated [Govindan & Bafna (230)], and the adsorption of aldehydes and ketones on cyanide anion exchangers was described [Gabrielson (231)]. Donnan membrane theory was applied to the adsorption of dyes by polymers and the effects of electrolytes on direct dyeing of the polymer were discussed [Kobayashi & Yoshikawa (232)]. Phenylenediamines in HCl solution were taken up by a Ca exchanger as nonpolar molecules as well as univalent ions. The exchange capacity of the resin was the same for ions of all three diamines, three toluidines and aniline [Davydov & Skoblionok (233)].

Industrial applications of ion exchange in concentration, purification and recovery processes were widely reported. Illustrative examples are furnished in the reported ion exchange extraction and concentration of U from 180 tons of ore [Hancher, Higgins & Taylor (234)]; a mixed bed process for the purification of low temperature tar acids [Depp & Neuworth (235)]; the use of an ion exchange slurry in radioactive decontamination of water [Lacy & Lind-

sten (236)]; and ion exchange processes for the recovery of base ions from waste sulfite liquor [Kasper & Katz (237)]. Remote control analysis of homogeneous reactor fuel by ion exchange methods was described [Horton, Thomason & Kelly (238)].

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MECHANICAL PROPERTIES OF HIGH POLYMERS[1]

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This review is concerned principally with the changes in shape of bodies when subjected to surface and inertia forces. The subject has been considered in part in previous reviews (1, 2, 3). In this report a general outline will be given of the present state of knowledge of the mechanical properties of polymeric systems, with references to some of the recent literature available to the author.

If we consider a small rectangular element in a body under stress, there will be normal and tangential tractions acting on the surfaces of the element. By suitably orienting the element, the three normal stresses can be made equal. The state of stress can thus be resolved into a hydrostatic stress, together with three sets of shear stresses. The former stress component causes changes in volume and the latter component, changes in shape. It is customary to consider separately the response to hydrostatic stress and to simple shear stress, and this procedure is followed in the present report.

With regard to the behavior under hydrostatic stress, there are two limiting values of strain associated with a given stress, corresponding respectively to very short and very long time-scales. We will consider first equilibrium behavior, and subsequently the kinetic aspect, or bulk viscoelastic behavior. Concerning shear behavior, two types of materials can be differentiated. In one type, no permanent change in structure results when the material undergoes a permanent deformation, and an experiment which results in a permanent deformation is repeatable. Such a material shows liquid behavior or flow. In the other type, the experiment is not repeatable after a body shows permanent deformation. Such a body shows solid-like behavior. Polymeric solids can be divided into two classes, rubberlike solids (which can be considered as polymeric liquids crosslinked into a giant network), and crystalline solids. In the former case the crosslinks may be small crystalline regions. It should be noted that materials showing crystalline solid behavior in shear at a given temperature, and also crystallite-crosslinked rubberlike solids, will show liquid-like behavior above the melting temperature.

In the case of polymeric liquids, at any given temperature we can observe two limiting types of behavior in shear. In experiments of sufficiently short time-scale, the mechanical behavior is approximately that of an ideal Hookean body, for which the elastic behavior is characterized by two independent elasticity parameters; in particular, the shear modulus is of the same order as the bulk modulus. In experiments of sufficiently long time-scale, the

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material behaves like a liquid, and it manifests a flow behavior which is Newtonian only for a vanishingly small rate of dissipation of mechanical energy. Under these conditions, the shear behavior is characterized by a single parameter, the viscosity. For intermediate time-scales at any given temperature, the response of a polymeric liquid at any given instant to shear stress is dependent not only on the shear stress at that instant but also on the previous stress history; this is called (shear) viscoelastic behavior.

If a polymeric liquid is cooled under conditions such that crystallization does not occur, it will manifest over a narrow temperature range a discontinuity in the rate of change with temperature of primary thermodynamic variables such as specific volume or heat content. This temperature region is called the glass transition T_g; below this region the material is said to be in the glassy state. Under these conditions the mechanical behavior for experiments of ordinary time-scale is approximately that of an ideal elastic Hookean body as specified above. It is often erroneously stated that the glass transition represents the temperature at which the mechanical behavior changes from that of a glass to that of a liquid. These types of behavior are ideal limiting ones, and the temperature at which any intermediate behavior is observed is dependent upon the time-scale of the experiment. Similar considerations apply to polymeric solids as discussed below.

In general, the steady flow behavior of polymeric liquids is non-Newtonian. In order to maintain steady flow behavior in simple shear of a polymeric liquid manifesting non-Newtonian behavior, normal stresses as well as tangential stresses are required. This phenomenon is often called the normal stress or Weissenberg effect.

Under conditions where the energy stored and rate of energy dissipation are small, the viscoelastic behavior is approximately linear. For linear viscoelastic behavior, rather general relations have been developed between the response in different types of tests in shear for a given material at a given temperature. These relations constitute part of the phenomenological theory of viscoelasticity. Rubberlike solids also manifest viscoelastic behavior in shear for intermediate time-scales; in this case the limiting behavior for very long time-scales is that of an ideal rubberlike solid, and not of a liquid. Many polymeric liquids manifest at an intermediate time-scale a behavior which approximates that of a rubberlike solid. Thus as the time-scale is increased at any given temperature, the behavior changes from that of a polymeric glass, through that of a rubberlike solid, to that of a liquid. Since the amorphous portions of a crystalline polymer manifest liquidlike and glasslike behavior at limiting values of time-scale, then for intermediate time-scales crystalline solids also manifest a viscoelastic behavior which is linear under the limiting conditions referred to previously.

If the stress on a particle of a body is not purely hydrostatic or simply a combination of shear stresses, then the body manifests viscoelastic behavior in both shear and volume. The phenomenological theory of viscoelasticity

has been extended to include such conditions for initially isotropic bodies; this theory of course deals only with behavior at a given temperature; the effect of temperature has to be taken into account either empirically or through molecular theory. The effect is more complicated in the case of crystalline solids, since changes in degree of crystallization may take place. Birefringence and dielectric behavior are sometimes closely related to mechanical behavior, and some recent work in these fields is referred to in this review.

EQUILIBRIUM ELASTIC BEHAVIOR OF SOLIDS

We first consider the equilibrium elastic behavior of rubberlike solids. The theory of large elastic deformations is due mainly to Rivlin, and experimental tests of the theory are due chiefly to Rivlin and collaborators. This work has been reviewed in part by Rivlin (4). If we consider, as before, a small rectangular element in a solid under stress, then in many cases the strain energy due to the hydrostatic component of the stress is negligible (as in simple tension) or is zero (as in simple shear). When we neglect the strain energy, if any, due to the hydrostatic stress, then the solid can be considered as incompressible. Let us assume that the orientation of a small rectangular block is chosen in the undeformed body so that after deformation the block remains rectangular. If λ_1, λ_2, λ_3, are the principal extension ratios of the block, then the first and second strain invariants are given by:

$$I_1 = \sum_1^3 \lambda_i^2, \qquad I_2 = \sum_1^3 1/\lambda_i^2$$

The theory of large elastic deformations of an incompressible solid states that the equilibrium strain energy per unit volume W of the deformed block is a single-valued monotonically increasing function of I_1 and I_2. The statistical theory as developed by various authors and put into this form by Treloar leads to a relationship of the form:

$$W = C_1(I_1 - 3)$$

where C_1 is a constant related to absolute temperature and the molecular structure of the rubberlike solid. This function is mapped out experimentally, for example, by two-way stretching of a thin sheet of rubberlike material. For this purpose, natural rubber vulcanized without fillers is suitable, since in experiments of ordinary duration at room temperature this material is in approximate elastic equilibrium. Experiments of this kind by Rivlin & Saunders (5) showed that the strain energy function is of the form:

$$W = C_1(I_1 - 3) + \phi(I_2 - 3)$$

where $\phi(I_2-3)$ is a function of I_2 such that $\partial W/\partial I_2$ decreases with I_2 at constant I_1. The disagreement between the statistical theory and experiment is demonstrated by plotting $f/2(\lambda-\lambda^{-2})$ against $1/\lambda$, where f is the tensile

force in a simple extension experiment divided by the original cross-sectional area, and λ is the extension ratio in the direction of the tensile force. Over a range of values of λ, straight lines of nonzero slope are obtained (5, 6). If a vulcanized rubber is swollen to a volume fraction v_2, a plot against $1/\lambda$ of the quantity $fv_2^{1/3}/2(\lambda - \lambda^{-2})$, where f is referred to the unswollen area, again gives straight lines, the slopes of which depend only on v_2 (7). For a value of v_2 equal to 0.20, the preceding quantity is independent of $1/\lambda$, in agreement with the statistical theory. This does not imply that the elastic behavior of highly swollen rubber is in agreement with the statistical theory, since a tension test represents a line on the strain energy surface $W = f(I_1, I_2)$, and nothing is known about the nature of the surface for swollen rubbers (8).

A valuable review of the present status of the theory of large elastic deformations has been given by Treloar (9); he points out that except for a proposal by Thomas (10), existing modifications to the statistical theory do not agree with experimental data. A series of natural rubber vulcanizates with a chemically determined degree of crosslinking has been prepared by Moore & Watson (11). The density of crosslinking, estimated from swelling measurements, was found to differ by a constant amount from the chemically determined value; this was attributed to the existence of entanglements. Another material which is approximately in elastic equilibrium in tests of ordinary time-scale at room temperature is crosslinked polydimethylsiloxane. Experiments by A. M. Bueche (12) on the elastic behavior of such polymers quantitatively crosslinked by high-energy radiation indicate that in this case also entanglements exist between the polymer chains.

It is well known that the rigidity of a vulcanized rubber is greatly increased by the presence of crystallites or rigid filler particles. An investigation by A. M. Bueche (13) on the effect of filler particles on the increase in rigidity of silicone rubber leads to the conclusion that this increase is due primarily to polymer-filler attachments. A theory for the rigidity of a rubberlike polymer containing crystalline regions has been developed by F. Bueche (14). He has found good agreement with his own data on two specimens of polyethylene and with the data of Leitner (15) on raw rubber.

An experimental survey has been made by Maxwell & Matsuoka (16) on the response at elevated temperatures of polystyrene and other polymers to hydrostatic stress. In the case of polystyrene, the compressibility changed from a low value characteristic of the glassy polymer at a pressure which increased with temperature. Complicated hysteresis and time-dependent effects were observed. The compressibility of several crystalline polymers has been calculated by Brandt (17), and he has obtained satisfactory agreement with experiment.

STEADY STATE BEHAVIOR OF LIQUIDS

The steady state response of polymer liquids to shear stress, or flow, is characterized by the viscosity at vanishingly small rates of shear, as men-

tioned previously. The problem is to determine theoretically and experimentally the dependence of viscosity on temperature, structure of the molecule, molecular weight, and molecular weight distribution. This subject has been recently reviewed by Fox, Gratch & Loshaek (18). Our knowledge of the dependence of viscosity on molecular weight of systems containing linear molecules is due mainly to the experiments on polystyrene and polyisobutylene by Fox and Flory, and the subsequent examination of previously published data by Fox & Loshaek (19). The relation between viscosity η and weight-average chain length Z_w is given by:

$$\log \eta = 3.4 \log Z_w + K$$

where K is a function of temperature, provided that Z_w is above a critical value dependent on the system. For fractions of chain length less than the critical value, the viscosity varies as a lower power of the chain length, approximately 1.7 for polystyrene and polyisobutylene; for disperse polymers in this molecular weight range, the viscosity is not a function of Z_w.

In the case of concentrated solutions of polymers, the molecules are entangled to a certain extent, as in a pure linear polymer. Additional complicating factors in this case are concentration and nature of the solvent. Recently, data have become available on the viscosity behavior of concentrated solutions of cellulose trinitrate (20), sodium deoxyribonucleate (SDNA) (21), and cellulose tributyrate (22). Earlier data have been discussed by Fox, Gratch & Loshaek (18).

A study has been made of the effect of branching on the dependence of viscosity on molecular weight in polyethylene by Peticolas & Watkins (23). Linear polyethylene was found to obey the above relationship; for branched polyethylenes, however, lower viscosities were obtained. It was found that the relation between viscosity and Z_w could be fitted to an empirical modification of the above equation taking into account the number of short chain branches. F. Bueche (24) has recently modified his previous theory to account for the 3.4 power dependence on molecular weight of the viscosity of linear polymers and concentrated solutions.

Temperature dependence of viscosity.—Until recently, the dependence of the logarithm of viscosity of polymers of high molecular weight on temperature was represented by a relationship involving an inverse integral power of absolute temperature. This power varies from two for polyisobutylene to 13 for polymethyl methacrylate (18). These relationships appear to hold over a wide range of temperatures.

More recently, Williams, Landel & Ferry (25) have proposed a universal relationship for the temperature-dependence of rheological and other time-dependent phenomena. Now it can be shown from molecular theories of viscoelasticity discussed subsequently in this article that the time-dependent part of the shear creep compliance at time t multiplied by $\rho T / \rho_s T_s$ is a single function of $t a_T$ where

$$a_T = \rho_s T_s \eta / \rho T \eta_s$$

In the above equation, ρ_s and η_s are the density and viscosity at an arbitrary reference temperature T_s, and ρ and η are the values at a temperature T. The temperature dependence of viscosity is then given by the universal relationship (25):

$$\text{og } a_T = \frac{-900 \ (T - T_s)}{C_2(C_2 + T - T_s)}$$

where C_2 is an arbitrary constant. In particular, values of C_2 equal to 51.6 and 101.6 correspond to values of T_s which lie respectively close to the glass transition temperature T_g and about fifty degrees C. above that temperature. The above relation involving T_g led Williams, Landel & Ferry to considerations of viscosity as a function of free volume (25). They find that log (η/η_g) is given by an expression of the form of the right-hand side of the preceding equation with T_s replaced by T_g, and with the viscosity at T_g given by η_g. Now the density ratio in the expression previously given for a_T is close to unity, hence this may be redefined as

$$a_T = T_s\eta/T\eta_s$$

Values of T_s for C_2 equal to 101.6 for a wide variety of systems, both polymeric and nonpolymeric, have been given by Williams, Landel & Ferry. It would be expected that if the temperature factor also is omitted, then there would be a slight change in the values of T_s required to fit the empirical expression with the same value of C_2. The significance of the parameters arising from the free-space derivation of the temperature dependence on viscosity has been discussed by the previously named authors (18, 25). An extension by F. Bueche (26) of his previous theory for mobility near T_g leads to an expression for a_T of the form given above. Fox, Gratch & Loshaek have proposed semiempirical relationships based on existing theories for the temperature and molecular weight dependence of viscosity for both the low molecular weight and the high molecular weight regions (18).

VISCOELASTIC BEHAVIOR OF AMORPHOUS SYSTEMS

Viscoelastic behavior is concerned with the mechanical response when the time-scale is such that the behavior lies between the limiting conditions discussed in the introduction. When the energy stored and rate of energy dissipated are small enough, the behavior approximates to ideal linear behavior. From the phenomenological theory of linear viscoelastic behavior, rather wide general conclusions can be drawn concerning the response at a given temperature of a system in different types of tests. First, we refer to what may be called a "one-dimensional scalar" theory. This applies to one specified type of stress and one specified type of strain, for example, tensile stress and longitudinal strain. It is applicable to any body, crystalline or amorphous, oriented or isotropic, provided only that the behavior is linear. This one-dimensional theory, which is analogous to the corresponding theory of dielectric behavior, has been summarized by Gross (27). This theory indicates

how different types of tests with the same or different time-scales may be related to each other. It can be used, for example, to study the effect of temperature on viscoelastic behavior by means of such relationships. The theory indicates that the experimentally observed viscoelastic behavior may be most conveniently represented by either of two equivalent spectra, the retardation spectrum or the relaxation spectrum (28).

In the case of initially isotropic bodies, the viscoelastic behavior at a given temperature can be represented completely by two independent spectra. These are most conveniently taken as either the retardation or relaxation spectrum for shear and for volume viscoelasticity (28). The relations for this complete theory of viscoelasticity have been discussed by Mandel (29), Schwarzl (30) and Staverman & Schwarzl (31). The phenomenological theory, of course, gives no information concerning the nature of the retardation or relaxation spectra, nor of the temperature dependence of viscoelastic behavior; molecular theories which have been proposed are discussed below.

Dilute polymer solutions.—We consider first dilute polymer solutions, in the concentration range where the molecules do not overlap, and we will discuss the shear viscoelastic behavior of such systems. The first successful calculation of the viscoelastic behavior of a dilute polymer solution is due to Rouse (32). He assumed that the polymer molecule was divided into a large indeterminate number N of segments; the length of each segment was such that it had Gaussian characteristics. From calculations of Treloar (33) this requires as few as five bonds for a freely rotating polymethylene chain. The energy loss resulting from the detailed flow mechanism (according to Eyring) of a segment through the medium is replaced by a frictional force represented by a friction factor f; this force is assumed to act at the junctions of the segments. The theory leads to a line relaxation spectrum for a dilute solution of a monodisperse polymer.

From this spectrum several results can be obtained from the phenomenological theory. In this connection, a detailed comprehensive discussion of this theory and other molecular theories has been given by Ferry (34). Since the viscosity can be calculated from the spectrum, the storage modulus $G'(\omega)$ can be calculated in terms of molecular weight, concentration, and intrinsic viscosity. As would be expected from a "free-draining" molecular theory, the intrinsic viscosity is found to be proportional to molecular weight. An experimental test of this theory was made by Rouse & Sittel (35). They obtained excellent agreement, except for the discrepancy noted above. It should be emphasized that N and f disappear in the final result, which thus involves no indeterminate parameters. The success of this approach has led to further developments, both theoretical and experimental. Zimm (36, 37) has obtained the line relaxation spectrum for a dilute solution of "nonfree draining" molecules, and has obtained a spectrum which is somewhat different from that for "free-draining" molecules; the correct expression for intrinsic viscosity is obtained. A model with an "internal viscosity" has

been discussed by Cerf (38, 39); he does not, however, give explicit results for the viscoelastic behavior of this model. A general review of this type of theory has been given by Zimm (40). New methods of measuring the visco-elastic behavior of dilute polymer solutions have been described by Zimm (41) and by Cerf and associates (42, 43).

High molecular weight amorphous polymers.—We will now consider the other extreme case, namely, amorphous systems containing only long mole-cules. The shear viscoelastic behavior can be characterized either by the response to stress or strain in step-function experiments or in dynamic experi-ments. The shear relaxation modulus $G(t)$ as a function of time is approxi-mately the mirror image of the shear storage modulus $G'(\omega)$, and one can be calculated from the other. The same is true for the elastic part of the shear creep compliance $J(t) - t/\eta$ and the shear storage compliance $J'(\omega)$. For polymers of sufficiently high molecular weight, these curves contain a pla-teau. It can be deduced that for the time-scale of the plateau, the system be-haves approximately like an ideally elastic vulcanized rubber; hence points of entanglement exist, which act like temporary crosslinks up to this time range. For shorter times or higher frequencies, over the transition range from glasslike to rubberlike behavior, the modulus curve is independent of molecular weight. The length of the plateau is very molecular weight-de-pendent, the transition from rubberlike to liquidlike behavior occurring at shorter times or higher frequencies at lower molecular weights.

In practice, it is not possible to obtain the whole significant range of the response curves at a single temperature, since they cover a large number of decades of time or frequency. It is usual therefore to make measurements over a range of temperature, and reduce these to a single temperature. Thus a set of stress relaxation experiments, which usually involve long time scales, can be quantitatively related to a set of dynamic experiments carried out with shorter time-scales over a somewhat higher range of temperature.

The first point which arises is that this comparison can be made over the whole range only for the same type of deformation. For example, stress re-laxation experiments are usually made in simple extension, and the results of such experiments are compared with dynamic experiments in shear. Now the phenomenological theory tells us that the viscoelastic moduli and com-pliances are related to each other in the same way as the corresponding mod-uli and compliances of classical elasticity theory; it is merely necessary in the case of dynamic experiments to replace the moduli and compliances by their complex equivalents, and in the case of step-function experiments by their Carson transforms (28 to 31). Thus, for example, there is no simple rela-tionship between the longitudinal storage modulus $E'(\omega)$ calculated from tensile stress relaxation data and observed values of $G'(\omega)$ in the region where $G'(\omega)$ and $E'(\omega)$ are approaching their upper limiting values where they are of the same order of magnitude as the bulk modulus. The calculation of $G'(\omega)$ from $E'(\omega)$ has been discussed in detail by Catsiff & Tobolsky (44).

Ninomiya & Fujita (45) have calculated $E'(\omega)$ from their stress relaxation data on polyvinyl acetate and compared this curve with data of $3G'(\omega)$ obtained on another sample by Williams & Ferry (46). This is justifiable, since in this region the viscoelastic behavior is independent of molecular weight. Good agreement was found except in the region of the upper limiting value, where $E'(\omega)$ falls below $3G'(\omega)$, as expected from the phenomenological theory. The same result was found in the comparison of $[H_l(\tau)]/3$ and $H(\tau)$, where $H_l(\tau)$ and $H(\tau)$ are the longitudinal and shear relaxation spectra. Fujita & Ninomiya observed the same result in comparing $H_l(\tau)$ obtained from their stress relaxation data on polystyrene (47) with $3H(\tau)$ obtained by Grandine & Ferry by dynamic measurements (48).

There is not a generally accepted method of reducing data obtained over a range of temperature to a standard reference temperature. In this connection, it is of interest to review at this stage the present status of molecular theories for the viscoelastic behavior of such systems, and to deduce therefrom a suitable reduction procedure.

It has been proposed that theories of the Rouse type can be applied also to systems containing only low-molecular weight polymer molecules (34, 49). This leads to the result that $G'(\omega)/\rho T$ is a function of ωa_T, where a_T only depends on temperature. Thus the effect of change in temperature is to shift the curve of $G'(\omega)/\rho T$ along the $\log \omega$ axis. This theory does not apply in the region where $G'(\omega)$ approaches the limiting glass modulus, which is, of course, not proportional to absolute temperature. For a polydisperse polymer, the relaxation spectrum is the weight-average of that for each species. This leads to the result that the steady-state compliance J_e is given from the phenomenological theory by:

$$J_e = (2/5 \, \rho RT)M_z M_{z+1}/M_w$$

Hence $\rho T J_e$ should be independent of temperature. It is possible that the assumption of a weight-averaged relaxation spectrum always leads to molecular weight dependence of J_e of the above form.

F. Bueche (50) has developed a theory for the viscoelasticity of a linear polymer which does not correspond to the Rouse theory. From his result it can be shown that the quantity,

$$\rho T[J(t) - J_e]$$

where $J(t)$ is the shear creep compliance, is a single function of t/α_T, where a_T is, as before, dependent on temperature. In a similar way, $\rho T[J'(\omega) - J_e]$ and $\rho T J''(\omega)$ should be functions only of ωa_T. Hence the effect of change in temperature is only to move the time-dependent part of the compliance, multiplied by ρT, along the $\log t$ or $\log \omega$ axis. In order to reduce data on relaxation or storage modulus to a standard temperature in the vicinity of T_g, it is thus necessary first to convert the modulus data to compliance data, then to perform the reduction as indicated, and to convert back to modulus. This

is easily done in the case of dynamic data if information on both $G'(\omega)$ and $G''(\omega)$ is available. This is more difficult with relaxation modulus data, and in this case it is usually assumed that the effect of change of temperature on $G(t)$ is simply to change the time-scale. The effect of omission of the density factor is usually negligible. It appears that the same is true if the absolute temperature factor is neglected; Fujita & Ninomiya obtained the same values of a_T for polyvinyl acetate (45) and for polystyrene (47) as did Ferry and associates (46, 48), who used the more complicated shifting procedure. The relation between temperature and time-scale is given in general by the expression for a_T referred to previously (25).

A critical test of the correct temperature reduction scheme would be in the plateau region of the response curve for a material which has a long flat plateau. The high molecular weight natural rubber fraction examined by Zapas, Shufler & De Witt (51) appears to satisfy these requirements. From their reduced values of $G'(\omega)$ it appears as if the temperature factor should be omitted; these authors have suggested that the usual superposition procedure might require modification.

Intrachain relaxation theories of the Rouse type do not, of course, account for the plateau in the response curves of high molecular weight amorphous systems. This can be incorporated into such a theory by consideration of the effect of entanglements on the friction factor f, as has been done by F. Bueche (52) and by Ferry, Landel & Williams (49).

An alternative approach to the viscoelasticity of a high molecular weight amorphous polymer is as follows: for the glass-rubber transition region, the material behaves as if the temporary entanglements were permanent crosslinks. For this region, theories of the viscoelasticity of networks have been developed by F. Bueche (50), Nakada (53), and Miyake (54). These theories lead to a linear relation between $\log H(\tau)$ and $\log \tau$ of slope $-1/2$, the so-called "wedge" relaxation spectrum, as originally proposed by Tobolsky (55), in agreement with experiment. In the transition region from rubberlike to liquidlike behavior, we can consider the temporary junction points as breaking and reforming in new positions. A theory of viscoelasticity based upon this model has been developed by Yamamoto (56). Mention should be made finally of a molecular theory of Ham for the viscoelasticity of linear branched, and crosslinked systems (57).

Effect of molecular weight distribution.—The tail end of the relaxation spectrum, corresponding to large values of time for the relaxation modulus or low frequencies for the storage modulus, is dependent upon the molecular weight distribution. It appears that with certain assumptions the molecular weight distribution can be obtained from the relaxation spectrum. Fujita & Ninomiya assume that the tail end of the relaxation spectrum for a monodisperse polymer is a rectangular "box," and that for a polydisperse polymer the tail becomes the weight-average of the individual species (45, 47). They obtained good agreement except at the low molecular weight end for both

polystyrene and polyvinyl acetate between the calculated molecular weight distribution and the distribution obtained from fractionation. A similar calculation for the NBS standard polyisobutylene gives reasonable results for the viscosity-average and weight-average molecular weights (58). Ninomiya (59) has further explored the possibilities of this method with various alternative assumptions concerning the spectrum of a pure species. The assumption of linear superposition has been tested by means of stress relaxation experiments on blends of fractions. It was found that the assumption did not hold when the ratio of molecular weights of the fractions was large (60). A similar experimental study has been made by Watkins, Spangler & McKannan (61) on the stress relaxation behavior of concentrated solutions of rough fractions of polymethyl methacrylate. The molecular weight distribution calculated from stress relaxation data agreed well with a Schulz distribution corresponding to the measured molecular weights.

It is well-known that the steady-state shear elastic compliance J_e, which is a measure of the energy stored in steady flow, is very dependent upon molecular weight distribution. The magnitude of this quantity is greatly increased when a small amount of high molecular weight polymer is added to low molecular-weight material. We have previously given the theoretical result due to Ferry, Williams & Stern (62). This was obtained from the assumption of weight-average superposition of Rouse spectra for each species. It is not clear whether this assumption should be valid for a high molecular weight polymer. Measurements of J_e have been made by Watkins on concentrated solutions of whole polymers, rough fractions, and of a blend of polymethyl methacrylate (63). For the whole polymers and fractions M_z and M_{z+1} were estimated from measurements of M_n and M_w; good agreement was obtained with the theoretically predicted values of J_e. In another investigation (64), measurements of J_e were made on a series of blends of two rough fractions of polyisobutylene. The higher molecular weight averages were obtained by direct measurement in an equilibrium ultracentrifuge under appropriate conditions. In this case, J_e was found to vary as $(M_z M_{z+1}/M_w)^2$.

Effect of chemical structure on shear viscoelastic behavior.—Previously published papers have been reviewed by Ferry (65); we will consider here more recent publications. Now that the basic principles and procedures for the specification of viscoelastic behavior are known, the interest at present is in the relationship between chemical constitution and viscoelastic behavior. Papers have appeared on crosslinked systems (specifically, vulcanized rubbers), on polymers with different backbone structure, on polymers with side-groups, and on concentrated solutions and gels of cellulosic polymers.

Interesting results have been reported on raw natural rubber (66) and on several vulcanized rubbers (66, 67) by Fletcher & Gent and by Payne. The data on raw natural rubber are in agreement with those due to Zapas, Shufler & De Witt (51) discussed previously; the same difficulty was observed in determining shifting factors in the plateau region. The relationship be-

tween the storage modulus curves for raw and vulcanized natural rubber is analogous to that reported by Brown & Tobolsky for vulcanized butyl rubber and polyisobutylene (68). Data are given for a vulcanizate of butadiene-styrene and other elastomers, and also on the effect of fillers (66). Data have been reported by Catsiff & Tobolsky (69) on the relaxation modulus $E(t)$ over the whole glass-rubber transition range for a vulcanized natural rubber; for comparison, earlier data on a vulcanized GR-S are also given. F. Bueche (70) has reported data on the longitudinal creep compliance of raw and vulcanized natural rubber, GR-S, and *cis*-polyisoprene.

The viscoelastic behavior of a network polymer, polyurethane, has been reported by Landel (71). The dynamic behavior of polyhexene-1 appears to be similar to that for polyisobutylene (72). Becker & Oberst give dynamic response data on several crosslinked and filled polymers (73). This viscoelastic behavior of copolymers and polymer mixtures has been reported by Jenckel & Herwig (74).

In addition to the main viscoelastic mechanism discussed above, a secondary mechanism is observed in polymers containing side groups. The apparent activation energy for this secondary process is less than for the main process. At low temperatures, in practice below the glass transition, the time-scale for the secondary process is much shorter than for the primary mechanism. At higher temperatures these two processes might be expected to occur in the same frequency or time-range. This has in fact been observed by Ferry and associates in a systematic study of the dynamic response in the glass-rubber transition range of a series of methacrylate polymers with different side groups (75 to 77). The temperature-dependence a_T of the main process was given by a function of the form referred to previously; however, for the three polymers, somewhat larger values for the numerical parameter are found. The temperature dependence of the secondary process was represented by a constant activation energy of the order of 20 kcal., decreasing with increase in side-chain length (77). The retardation spectra due to the secondary maximum for two of the polymers have been compared to that for polymethyl methacrylate (76). The dielectric behavior of two of these polymers has been reported by Strella & Zand (78).

In order to obtain complete information concerning the effect of side-groups, it is desirable to make measurements over a range of frequency and temperature; such data have been reported for polymethyl methacrylate by Maxwell (79). Since such experiments are time-consuming, it has been the practice to make measurements over the significant temperature range at a single frequency which is only approximately constant. In this way, a large number of materials can be surveyed rapidly. Data on secondary viscoelastic processes obtained in this way have been recently reported by Wolf & Schmieder (80), Heijboer (81), Sauer *et al.*, (82, 83), and Butta (84). Of particular interest appears to be the effect of short-chain branching in polyethylene. In addition to affecting the degree of crystallinity, these short side-branches give rise to a characteristic secondary viscoelastic process. Data

have been reported on systems containing stiff molecules, namely, solutions and gels of trisubstituted cellulose esters (85, 86, 87) and solutions of sodium desoxyribonucleate acid (SDNA) (88).

Other investigations.—A study was made by Smith on the NBS standard polyisobutylene (89). He obtained tensile stress-longitudinal extension curves over a wide range of rates of elongation and temperature, and showed that these data could be reduced to a master curve for 25°C. corresponding to unit strain rate. The shear relaxation modulus $G(t)$ calculated from this master curve agreed with published data. Onogi & Ui (90) have shown that if a reasonable assumption is made for the shape of the relaxation spectrum, then isothermal dynamic response data for a range of frequencies can be successfully predicted from data obtained at a single frequency over a range of temperature.

Volume viscoelasticity.—The existence of volume viscoelasticity in the NBS standard polyisobutylene was demonstrated by comparing values of $G^*(\omega)$ reduced to 25°C. with values reduced to the same temperature of $K^*(\omega)+(4/3)G^*(\omega)$ obtained from longitudinal plane wave propagation (91). Cunningham & Ivey (92) have developed a method for the measurement of $G^*(\omega)$ at high frequencies, and compared data on several vulcanized rubbers with previous data on $K^*(\omega)+(4/3)G^*(\omega)$. They conclude that $K''(\omega)$ is negligible compared to $G''(\omega)$ for vulcanizates of GR-S and natural rubber, but not for those of other elastomers. Data on $E^*(\omega)$ and $G^*(\omega)$ for various rubberlike systems are given by Koppelmann (93). In the above methods, $K^*(\omega)$ is obtained by taking the difference between two sets of experimental data. A direct method for the determination of $K^*(\omega)$ has been developed by McKinney, Edelman & Marvin (94).

VISCOELASTICITY OF CRYSTALLINE POLYMERS

The viscoelastic behavior of crystalline polymers is more complicated than that of amorphous systems, and relatively little is known about this behavior. Much of the work on crystalline polymers has been on oriented specimens in the form of fibers, and this introduces additional complications. At any given temperature, the amount of crystalline material, and the size and arrangement of the crystalline units are not fixed quantities, hence the viscoelastic behavior of a crystalline polymer at a given temperature is not a single-valued function of time or frequency, as with amorphous systems. A further difficulty is that the viscoelastic properties of many crystalline polymers of interest are moisture-sensitive. These complications were avoided in a study by Fujino, Kawai & Horino (95, 96). These workers made measurements of $E'(\omega)$ and $E''(\omega)$ on textile fibers over a wide range of frequencies at constant temperature and relative humidity. By making use of several types of apparatus, six decades of frequency were covered. Measurements following a similar scheme have been reported by Tokita (97).

An unusual viscoelastic phenomenon has recently been reported by Fitzgerald (98). Measurements of $J^*(\omega)$ on several crystalline polymers at

closely spaced frequencies have revealed the existence of narrow dispersion regions of the resonance type. In contrast to the usual relaxation dispersion behavior, in which $J'(\omega)$ decreases monotonically with increase in frequency, sharp maxima followed by sharp minima were observed, including in one case a negative value of $J'(\omega)$. Fitzgerald has pointed out that such behavior can be represented to a first approximation by the usual four-element linear model with added series mass. Measurements were made over a narrow range of temperature above the room-temperature transition in Teflon. The parameters of the spring and dashpot of the Voigt element in the equivalent model were unchanged by temperature, while the series mass decreased with increase in temperature with an "activation energy" of 13.2 kcal. By analogy with a similar behavior he observed in metals, Fitzgerald tentatively ascribed this resonance absorption to dislocations in the crystallites.

Resonance absorption has been discussed from the phenomenological point of view by Pelzer (99) and Gross (100). Such an absorption is required to account for frequency-independent $J'(\omega)$ or $\epsilon'(\omega)$ occurring simultaneously with nonzero frequency-independent $J''(\omega)$ or $\epsilon''(\omega)$. Pelzer has proposed a ladder model containing only springs and masses.

We now consider the possibility of obtaining the relaxation spectrum over a wide range of times from measurements at several temperatures, as with amorphous systems. First, the melting range may extend considerably below the melting temperature; second, the longer time-scale for stress-relaxation experiments compared to that for dynamic experiments permits the data to be obtained in a lower range of temperature. Hence it should be possible to obtain the relaxation spectrum by stress-relaxation experiments of sufficiently long duration at sufficiently low maximum temperature. According to stress relaxation measurements on polyethylene (101) and poly-trifluorochloroethylene (102), such measurements require very long times for these materials. This procedure has been successfully applied to measurements of torsional stress relaxation in a nylon 6 fiber (103). By combination of measurements obtained at 0 per cent and at 75 per cent relative humidity, the relaxation spectrum over twenty-one decades was obtained. A similar study has been made on polytetrafluoroethylene (104). Data obtained respectively above and below 20°C. could be separately reduced with different shifting factors to two smooth master curves at 20°C. In this way the spectrum over fifteen decades of time was obtained.

Low-temperature dielectric constant measurements have been made on dry cotton and regenerated cellulose (105), and normalized data were reduced to master curves according to the method of Ferry & Fitzgerald (106). From the unique shifting factor curve for all the materials tested, the apparent activation energy for dielectric relaxation was found to have a sharp maximum at −21°C. In line with rheological observations in amorphous systems, this temperature must be close to the glass transition for the amorphous component of dry cellulose.

Longitudinal creep and recovery measurements on isotropic cellulose

films have been reported by Van Holde (107). These results are in agreement with earlier results on oriented cellulose fibers (108). Since such materials are solids, the observed permanent deformation is not of the nature of flow. The viscoelastic behavior of the isotropic films was found to be very non-linear with stress, hence the previously observed nonlinearity in fibers must be due to their polycrystalline nature and not to their anisotropy.

Earlier data on oriented crystalline polymers have been reviewed by Van der Vegt (109). Dynamic data on crystalline polymers are found in previously quoted papers (79 to 84). The dynamic behavior of nylon-type polymers has been reported (110, 111).

Phenomenological Theory of Viscoelasticity

Ladder mechanical networks, analogous to ladder electrical networks which are well-known in electrical circuit theory, have been discussed by Gross & Fuoss (112, 113). Gross has shown (113) that the relaxation spectrum derived by Rouse for a noncrosslinked polymer (32) and the retardation spectrum derived by F. Bueche for a crosslinked polymer (50) correspond to the same ladder model, and hence these spectra are equivalent to each other. The same result was deduced by Ferry by a different method (34). Gross (114) has discussed electrical analogs for viscoelastic systems. Hopkins & Hamming (115) have developed a method for the calculation of creep compliance from relaxation modulus by means of the convolution integral of these functions discussed by Schwarzl (30). Fujita (116) has developed a new method of calculating higher approximations to relaxation spectra from dynamic measurements. This method gives a complete series of approximations from both the storage modulus and the loss modulus.

Lee & Morrison (117) have discussed the propagation of waves along rods, the viscoelastic properties of which are represented by certain simple models. Bland & Lee (118) showed how to obtain numerical values of the parameters for such models to fit actual dynamic response curves over a specified limited range of frequency. Kolsky (119) has demonstrated that the measured shape of stress pulses propagated along a rod of polymeric material agrees with the shape calculated from the longitudinal storage and loss moduli.

Three-dimensional viscoelasticity theory has been reviewed in references given previously (30, 31) and by Leaderman (120). The subject has been discussed from the viewpoint of operator equations by Alfrey & Gurnee (121). The problem of the calculation of stress and deformation in a body manifesting both volume and shear viscoelasticity has been discussed by Lee (122, 123). Biot has treated the viscoelasticity of anisotropic bodies (124).

Non-Newtonian Flow

As mentioned previously, the ratio of shear stress to rate of shear for a polymeric liquid in steady flow is not constant, but is a function of rate of shear; this behavior has been reviewed by Hermans in this series (3), and

also by Pao & Brandt (125). Non-Newtonian flow arises, at least in the case of dilute polymer solutions, as a result of simultaneous rotation and distortion of the molecule. Pao (126) has shown that the rotation of viscoelastic elements in a stress field leads to non-Newtonian flow behavior, and he has given the apparent viscosity in terms of the retardation and relaxation spectra. This theory predicts that a Maxwell body should not show non-Newtonian flow. A previous treatment of this type by De Witt (127) led on the other hand to non-Newtonian flow for such a body. This theory predicted that the apparent viscosity η_a as a function of rate of shear should give the same curve as dynamic viscosity $G''(\omega)/\omega$ as a function of ω. The Pao theory on the other hand predicts equivalence between the apparent fluidity $1/\eta_a$ and the dynamic fluidity $\omega J''(\omega)$. Thus in the former comparison, $G''(\omega)/\omega$ should fall faster than η_a, which it, in fact, does (128). This theory also predicts that the elastic recovery should decrease with increase in rate of shear, and this is known to be the case (129). The theory predicts that the elastic recovery as a function of rate of shear should be identical with $J'(\omega)$ as a function of ω. This theory was used to calculate from the retardation spectrum the apparent viscosity and flow through a capillary of a sample of polyethylene, and good agreement with experiment was found.

Pao (130) has obtained the same result by modifying Zimm's treatment, and he has derived an expression for the relative intrinsic viscosity in terms of Zimm's spectrum discussed earlier (36). He has found good agreement with previously published data.

Bueche, Wood & Wray (131) have examined experimentally the validity of Bueche's formula for the apparent viscosity as a function of rate of shear for a solution of free-draining molecules (132). They measured the apparent viscosity of several concentrated solutions, and could obtain a good estimate of molecular weight. In a subsequent work, Bueche & Harding (133) showed that, for a series of concentrated solutions of various specimens of polymethyl methacrylate, a unique curve of apparent viscosity against rate of shear was obtained; this curve differed somewhat in shape from the theoretical curve. From this experimental curve, molecular weights were obtained and found to be in good agreement with viscosity average molecular weights, except in the case of blends, which gave too high values of molecular weight.

Cerf (134) has extended his previous theory (39) to include rotation of the molecule, and obtained results for non-Newtonian flow in good agreement with experiment. Čopič has considered similarly a necklace-type molecule (135). As mentioned previously, for a concentrated solution or solvent-free system containing long molecules, a better representation is a rubber network model, the crosslinks of which break and reform. Yamamoto (136) has shown how such a model can lead to non-Newtonian flow.

Recent experimental studies on non-Newtonian flow behavior include measurements on polyethylene (137), and on solutions of polyisobutylene (138), natural rubber (139), sodium deoxyribonucleate (SDNA) (21), and cellulose nitrate (141).

Normal Stress Phenomena

When a system containing polymer molecules exhibits steady-state flow in simple shear, then the three components of the normal stress on the three mutually perpendicular planes associated with the plane of flow are not equal to each other; this is sometimes known as the "normal stress effect" or "Weissenberg effect." This behavior is found in other systems besides those containing long flexible molecules; it appears to be associated with non-Newtonian flow and certain flow birefringence phenomena, as discussed below.

During the past few years, several phenomenological theories have been proposed for the normal stresses, and there has been much discussion concerning the validity of these theories. The situation has been clarified by Markovitz (142), who has classified the theories on the basis of the relations predicted between the deviatoric components of the normal stress; he has listed the measurable quantities in terms of these components for three types of rheological instruments. He has also correlated published data on polyisobutylene solutions, and considered the validity of certain theories. Markovitz has also shown (143) that normal stress data on polyisobutylene solutions can be superposed in the same way as dynamic data, and that there is an empirical relationship between the normal stress effect and $G'(\omega)$. Normal stress phenomena have also been discussed by Philippoff (144), and data have been reported by Philippoff et al. on solutions of polyisobutylene (138, 145) and cellulose nitrate (141). Measurement techniques have been discussed by Roberts (146). From a molecular theory for a network with mobile junction points, Lodge has derived the normal stress and flow birefringence behavior (147).

Birefringence

Three types of birefringence behavior in polymers are studied, namely, the birefringence of elastically deformed rubberlike solids, birefringence associated with rheological or chemorheological phenomena, and the birefringence in polymeric liquids under steady flow. Aspects of birefringence phenomena have been reviewed by Peterlin (148), Stein (149), Treloar (150) and Saunders (151).

Saunders has carried out an investigation of the birefringence of stretched amorphous natural rubber and gutta-percha (152), and also of stretched amorphous polyethylene and polymethylene (153); he has discussed his data on the optical anisotropy of the equivalent random link (154).

The network theory of Lodge referred to previously (147) leads to the important results that the principal optical directions should coincide with the principal stress directions, and that the birefringence should be proportional to the difference in principal stresses. This prediction was verified by Philippoff (145, 155) on a concentrated solution of polyisobutylene. The principal stresses were obtained by separate measurement of shear and nor-

mal stress over a range of rate of shear, and the extinction angle and birefringence were measured over the same range. The stress-optical coefficient obtained was in agreement with published data on polyisobutylene. The same relation between birefringence and principal stress difference was subsequently found for solutions of lower concentration and for pure polyisobutylene (138). Further work on the flow birefringence of dilute solutions of cellulose nitrate showed that the stress-optical coefficient changed somewhat with concentration at low concentrations (141).

Owing to lack of space it has been necessary to omit, or to refer only briefly to, many important contributions.

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REACTION KINETICS AND MECHANISMS OF GAS PHASE REACTIONS[1]

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Introduction

Investigations of the kinetics of reactions that occur in gaseous mixtures vary markedly in their philosophies. At one extreme the sole interest is in the determination of the apparent rate of conversion of reagents to desired products as a function of concentrations and temperatures. At the other end of the scale, an obsession with details of a mechanism may lead the kineticist to forego rate determinations, per se, and concentrate upon other types of experiments. As a result, there are few topics of physical chemistry and fewer methods that fall outside the self-chosen province of the kineticist. This range of interests is indicated by the main topics that follow. The discussions are not inclusive, but are exemplary. Often, to focus attention on a subject, incomplete summaries of particular papers are given. For this apologies are due the authors but not the readers. To find all the gold they must explore the hills. An attempt is made to treat each topic independently. Fortunately, this fails. Were there no leakage through the barriers many of the problems would be insoluble and many others of limited interest.

Rate Theory

The major development in rate theory during the year concerned the calculation of the pre-exponential factors $(A, \Delta S^{\ddagger}$ or the partition function ratio) in the rate expressions for elementary bimolecular reactions (1):

$$k = A \exp\left(-E^*/RT\right) = kT/h \cdot \exp\left(\Delta S^{\ddagger}/R - \Delta H^{\ddagger}/RT\right)$$
$$= kT/h \cdot F^{\ddagger}/F_A \cdot F_B \cdot \exp\left(-E^{\circ}/RT\right)$$

1.

Last year, Herschbach *et al.* (2) presented a prescription for calculation of the partition function $(F^{\ddagger})$ of the activated state. Briefly, this employs a rational molecular model for the activated state, one in which (*a*) bond lengths, angles, and force constants identical with those of the reagents and products are assumed; and (*b*) the reaction coordinate is taken as an asymmetric stretching vibrational mode, about the atom which is transferred, for which the restoring force is set equal to zero. Then a vibrational analysis of this pseudomolecule is made and $F^{\ddagger}$ evaluated. The method, which depends in large part upon the techniques developed by the authors to permit a fairly detailed vibrational analysis of these hypothetical polyatomic molecules, reproduced the pre-exponential factors of twelve simple bimolecular reactions. In 1957 these authors, severally, have applied this method to sev-

eral types of reactions. Wilson & Johnston (3) calculated the factors for nine hydrogen atom abstraction reactions, with a good degree of success in eight cases. For these reactions linear activated complexes were assumed, known molecular parameters were employed, and the bonds involved in the H atom transfer were treated as half bonds with appropriate lengths and force constants derived from Pauling's and Badger's rules. Pitzer (4) tackled chlorine atom reactions and showed the great extent to which classical methods may be used to calculate partition function terms that involve either stretching modes for heavy atoms or low frequency bending modes. This further simplifies the problem. In the reactions of Cl with hydrocarbons all C—H bonds were assigned the same potential energy function and the Cl . . . H—C interaction was approximated from the model for Cl . . . H—H. The result for the methane-Cl atom reaction agreed with experiment within a factor of two.

This prescription was also applied to the interpretation of an experimental study of the carbon isotope effect in the reaction, $CO + NO_2 \rightarrow CO_2 + NO$, by Johnston, Bonner & Wilson (5). In this case there is some ambiguity concerning what would constitute the "best" force constants for the activated complex. The authors tried three sets and found one that reproduced the experimental data well. In this case not only the pre-exponential factors but the activation energy difference could be deduced.

Neither this approach to the calculation of rates, nor that employed by Slater for unimolecular reactions (6) is able to determine activation energies. Solution of this problem, which requires evaluation of the potential energy surface for the reaction coordinate, remains a formidable task. If anything, the requisite calculation for the simplest of reactions, $H + H_2 \rightarrow H_2 + H$, appears to become more complex with time (7). However, a limited model relating activation energies to bond strengths has had some success in the treatment of atom abstraction reactions. Trotman-Dickenson (8) suggested the relation,

$$E^* = \alpha D(R - H) - \beta \qquad 2.$$

for reactions of the following type, $R_1 + R_2 H \rightarrow R_1 H + R_2$, with α and β as constants. This expression, which is an outgrowth of the much earlier work of Polanyi (9) on sodium diffusion flames, has been tested for methyl radical abstractions of H and recently for trifluoromethyl radical reactions by Dodd (10). The reactions of paraffins with both CH_3 and CF_3 obey such relations with few exceptions. In addition, the reactions of these radicals with a number of organic compounds show a linear relation between the activation energies for abstraction by these two radicals.

While such rate-energy relations have proved to be invaluable in solution kinetics [Hammett plots (11)] they have not been applied widely to gaseous reactions, probably because of a lack of examples of closely related reactions. They may offer a simplified approach to the calculation of activation energies, once the factors α and β are understood. Even where an equation like

(2) is not usable at present, there is a need for the systematic study of related reactions in order to define the mechanism. An example is the study of pyrolysis of organic halides and esters, in which systematic variation of either the hydrocarbon residue or the functional group produces a systematic variation in the rates, thus indicating similar rate-controlling factors [Gordon, Price & Trotman-Dickenson (12)].

DISSOCIATION AND RECOMBINATION REACTIONS

Conceptually, a very simple reacting system is that composed of a large, nonreactive heat bath in which a few diatomic molecules are dissociating and the atoms are recombining. The former requires an accumulation of energy by collision from the heat bath and the latter a "third body" or nonreactive molecule to remove the energy released by bond formation. Estimates of recombination rates (or of dissociation rates, since if one is known the equilibrium constant for the reaction enables a prediction of the other) have rarely been precise, nor have those made by one chemist agreed well with another's. In recent years these difficulties have been circumvented either by using flash photolysis to produce high concentrations of atoms the recombination of which is studied, or by shock compressions to raise the diatomic molecules to a high temperature at which they then dissociate. Precision has not been improved by the use of these methods, but the range of experimental conditions has been extended so far that trends are easier to spot.

The present evidence concerning iodine and bromine is summarized here. Flash photolysis of iodine in excess argon and bromine in A, N_2, and O_2 has been used to produce atoms for a study of recombination rates below 175°C. [Strong et al. (13)]. If both processes follow the course, $X + X + A \rightarrow A + X_2$, then the rates are the same for both I_2 and Br_2, $k = 3.2 \times 10^{15}$ cc.^{2}/mole^2 sec. Nitrogen is slightly more effective than A as a third body, and oxygen is about 2 times as effective. (Iodine, as has been discussed in several recent papers on flash photolysis, is very efficient, up to 250 times more effective than A for I_2 formation; bromine is more effective than A, but to a much smaller extent than I_2.) Over this temperature range there appeared to be slight negative temperature coefficients: $E^* = -1.4$ (I_2 in A) and $E^* = -2.0$ kcal./mole (Br_2 in A). These values are consistent with earlier flash photolysis work, corrected for self-heating effects.

Shock tube studies by Britton & Davidson (14), Britton et al., (15) and Palmer & Hornig (16) provide data above 1000°K. The former authors found that the efficiency of iodine and bromine as third bodies was much lower in the high temperature region. Iodine recombination in argon showed a negative temperature coefficient of $E^* = -4.56$ kcal./mole in the high temperature region, but when these data and those for bromine were combined with low temperature flash photolysis results, lower but still negative activation energies resulted: $E^* = -1.33$ (I_2 in A) and $E^* = -1.45$ kcal./mole (Br_2 in A). While these coefficients are undoubtedly real, the greater values

obtained in the high temperature region in this work and in that discussed below cast doubt on the values.

Palmer & Hornig report dissociation rates for bromine in a $1:10 = Br_2:A$ mixture that was shocked to produce temperatures from 1200°K. to 2225°K. While recombination rates calculated from these studies are consistent with those obtained by Davidson, the striking feature is the low temperature coefficient for dissociation. Although the dissociation energy of Br_2 is 45.2 kcal./mole, the activation energy was found to be only 30.7 kcal./mole (Br_2 in A). To account for this, the rate constant was analyzed in terms of the following unimolecular rate expression:

$$k = [Z(E^0/RT)^{n/2} \exp(-E^0/RT)]/(n/2)! \qquad\qquad 3.$$

in which n indicates the number of internal degrees of freedom that can store or contribute energy in the process. On this basis nine degrees of freedom participate in the reaction complex. If the shock tube data are combined with the low temperature photolysis, either a low activation energy results, or four degrees of freedom must be invoked. The analysis would indicate the participation not only of vibrations but also rotations in the energy transfer process. While such extensive participation of available degrees of freedom is unlikely for Br_2 alone, four active degrees in a Br_2-A complex would be in line with the behavior of other systems that have been analyzed in terms of this theory. Problems of interpretation aside, it is noteworthy that in this system the reaction rate may be reproduced by one equation valid for a variation of a factor of 10^{27}, which is, surely, the record.

Several other combination studies have been reported. In the flash photolysis of ozone, discussed later with respect to energy transfer, a series of third-body efficiencies was determined by McGrath & Norrish (17) for the reaction, $O+O_2+M \rightarrow O_3+M$. On a relative scale these were what we have learned to expect, the efficiencies increasing with molecular complexity, except for SF_6, which, unaccountably, was scarcely more efficient than the inert gases. Ethyl radical recombination has been investigated by Shepp & Kutschke (18). The rotating sector photolytic technique was applied to diethyl ketone. The temperature range was from 50 to 150°C. The recombination rate constant was close to that for methyl radicals and showed $E^* = 2$ kcal./mole. The authors suggest that this barrier is due to the overlap of CH orbitals on the recombining carbons, that is, to "F" strain.

Wijnen (19) photolyzed methyl acetate at 29 and 70°C. The products indicate two primary processes and subsequent radical recombination and disproportionation, for which $E_1^* = 1.5$ kcal./mole and, at 70°, k_1 was greater than k_2 in the following reaction:

$$CH_3COOCH_3 \rightarrow CH_3CO + CH_3O$$
$$\rightarrow 2CH_3 + CO_2$$
$$CH_3O + CH_3 \rightarrow CH_2O + CH_4 \qquad\qquad k_1$$
$$\rightarrow CH_3OCH_3 \qquad\qquad k_2$$
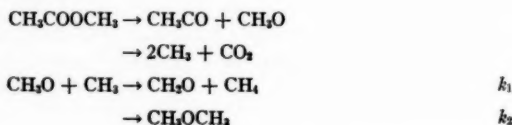
The low activation energy is not surprising for abstraction from a radical, but the higher efficiency is. In the same work the abstraction process, $CH_3O + CH_3COOCH_3 \rightarrow CH_3OH + CH_2COOCH_3$, showed $E^* = 4.5$ kcal./mole. It would be useful for comparison to have in hand data on abstraction from ethane or CD_4 by this radical.

Finally, combination reactions between boron trifluoride and the three methyl amines have been studied in a flow system in which mixtures of pairs of amines (in excess) were reacted with the fluoride [Daen & Marcus (20)]. The composition of the unreacted amine mixture was used to determine comparative rates. These are to be aligned with those obtained for the same reactions by the temperature pattern variant of the diffusion flame technique [Kistiakowsky & Williams (21)]. In neither case were the results precise—they rarely are with very rapid reactions. The competition experiments showed rate constants for reaction with mono-, di-, and trimethylamine to be in the proportions $1:5:12$, while, at slightly higher pressures the temperature pattern results were $1:5:8$. This correlation is good. The main variance between the two sets of results is that the competition experiments do not show any dependence of rate constant upon pressure while the other results do. However, the difficulties attendant upon the use of the competition method could account for this.

UNIMOLECULAR REACTIONS

The concept of a process in which a molecule first accumulates energy and then, after a finite time, rearranges or splits has been a fruitful one. The theory has been developed in great detail but is not yet entirely satisfactory. The current status of this theory was considered by Johnston last year (22).

Experimentally such reactions are elusive. Not only is the unimolecular character of a decomposition difficult to establish, but the rate must be evaluated with high precision over a wide range of pressures. As a result the useful test cases against which theoretical predictions may be checked are few and accumulate slowly.

The contributions in this field this year have been experimental. Weston (23) has extended our knowledge of the prime case, cyclopropane, by pyrolyzing cyclopropane-t to propylene-t. There is a tritium isotope effect on the rate constant, and also a C^{13} effect. In the following reaction the usual two step unimolecular mechanism predicts a decrease in reaction rate when the pressure (frequency of energy transfer processes) is decreased.

$$P + M \rightleftarrows P^* + M$$

$$P^* \rightarrow products$$
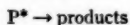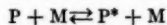
The observed isotope effects also decrease and may be restored by pressurizing with inert gas. The results agree with the more limited study by Lindquist & Rollefson (24). Unfortunately, no test of the relative merits of the Slater and Hinshelwood theories can be made using these data. The precision is too low to permit one to distinguish between the similar predictions. Nor

may a decision be made concerning the mechanism, whether a C—C bond rupture or a hydride shift is the initial act. The difficulty is mainly that, in the second possibility, the effect of one tritium atom is slight among that of five H atoms. We should look forward with great interest to reports on the pyrolysis of C_3D_6 or C_3T_6.

Cyclobutane shows most of the hallmarks of a unimolecular decomposition in its decomposition to ethylene. Ethylcyclobutane decomposes to ethylene and l-butene at an almost identical rate [Wellman & Walters (25)]. The reaction is homogeneous and, like cyclobutane and cyclopropane, is not inhibited by NO, propylene, or other approved free radical absorbers. The low pressure region, in which the rate constant should show the characteristic decrease, has not been determined for this reaction. In contrast to the possible hydride shift in cyclopropane, the behavior of these two alicyclic paraffins is easier to rationalize in terms of carbon-carbon bond scission. (Cyclopentane, which is discussed later, decomposes in a free radical chain process, not unimolecularly (73).)

While nitrogen pentoxide decomposition is complex, the first step is assumed to be a unimolecular split. Jach (26) studied the effect of inert gases upon the initial rate of N_2O_5 decomposition when NO was present in excess. Under these conditions the following reactions predominate:

$$M + N_2O_5 \rightleftharpoons NO_2 + NO_3 + M \qquad\qquad k_{1,-1}$$

$$NO + NO_3 \rightarrow 2NO_2 \qquad\qquad k_2$$
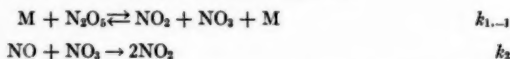
The observed initial rate is merely that of reaction (1). Once the experimental rate constant had been reduced by decreasing the total pressure of reagents, it could be restored to the same limiting high pressure value by CO_2, N_2, SF_6, CF_4, or NO. For CO_2 a total of 1600 mm. Hg was required to maintain the rate constant at the limit value while the N_2O_5 concentration was varied. The unimolecular nature of this process is substantiated, but the system does not seem suitable for a test of the subtleties of the theories. Hisatsune, Crawford & Ogg (27) have also studied this system, although not primarily for the elucidation of rate theory. They employed a rapid-scanning infrared spectrometer, and used this reaction for a test of this new tool. They worked with the system in the intermediate pressure range and determined k_1 and the ratio k_{-1}/k_2. The values of the former agreed with previous determinations, including an increase with pressure of both the activation energy and the pre-exponential factor. The ratio k_{-1}/k_2 also showed variations in these quantities with pressure, the activation energy difference decreasing and the pre-exponential factor ratio increasing with pressure. Such variations are presumably related to the time available for the redistribution of energy in an excited N_2O_5 molecule. The effect is definite for k_1, but for the ratio it is within the experimental error and the value may be an artifact.

Thermal activation (collision with a set of molecules in which a Boltzmann distribution of energies obtains) is postulated for all of the cases above. Decomposition following a large single stage energy input also falls within

the province of unimolecular mechanisms, provided that the decomposing entity survives long enough for an internal redistribution of energy to occur. This concept has been applied to mass spectral fragmentation patterns [Rosenstock *et al.* (28)]. Electron bombardment produces a parent ion with sufficient energy for bond fission. The resulting ion may also decompose. When the absolute rate theory formulation of unimolecular reactions is applied and appearance potentials are used to establish activation energies, an adequate interpretation of the mass spectra of methane, acetylene, and butane has been obtained (29–31). Results with alcohols are ambiguous (32). Particular emphasis in this work is placed upon the interpretation of weak, diffuse nonintegral mass peaks that are produced by metastable ions that decompose after being accelerated out of the ion-chamber but before entering the magnetic analyzer. These decompositions are predicted to be identical with those that occur within the ion chamber, and, therefore, they indicate important elementary decomposition steps. Experimentally this field is in its infancy, but it offers a direct approach to the study of intramolecular energy distribution and bond scission.

Intermolecular Energy Exchange

In any decomposition process, or in exothermic bimolecular reactions, it is possible to form the products in excited electronic or vibrational states. The subsequent behavior of such species does not affect the progress of the reagents along the reaction coordinate, but it does bear on the inverse process of activating a molecule before decomposition. In addition, the effect of excitation energy upon chemical reactivity must be considered.

At present our knowledge of this field is fragmentary. The bearing of mass spectral fragmentation studies on such problems has been mentioned. Ultrasonics, flash photolysis, and atom reaction experiments all provide information. Put very briefly, translational and rotational energies equilibrate quickly upon collision, but the transfer of vibrational energy to other modes is slow. A symposium held in September 1956 by the American Chemical Society summarized the status of the problem to that time (33–37).

The slow equilibration of vibrational energy is important because it is in these degrees of freedom that the chemical energy released upon the formation of a bond will first appear. The slowness of this process also means that the loss of energy by radiation can compete with it. Thus it is feasible to study the formation and decay of excited molecules by analysis either of their emission or absorption spectra. A theoretical analysis of the deactivation of vibrationally excited molecules has been made by Montroll & Shuler (38), Rubin & Shuler (39), and Bazley *et al.* (40). They treated the behavior of a set of oscillators (harmonic or Morse oscillators) that may lose energy either by collision or radiation after some specified initial excitation. For certain special excitation conditions the relaxation behavior has been evaluated. The harmonic oscillator is a reasonable model for interpretation of vibrational relaxation, the contribution of anharmonic terms being small.

Windsor, Davidson & Taylor (41) reported on the rate at which the second excited vibrational level in CO was populated after a shock compression raised the system to a high temperature. They monitored the infrared emission between 2 and 2.8 microns, corresponding to the following transition:

$$CO(V = 2) \rightarrow CO(V = 0) + h\nu$$
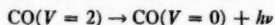
The mechanism of populating the second level appeared to be by absorption of one vibrational quantum at a time. The rate deduced for the transition at one atmosphere and $1470°K$. was $k = 5 \times 10^4$ sec.$^{-1}$ in dry CO, and was much larger in moist gas. Extension of this method to permit monitoring of several bands would assist in the assessment of the relative importance of radiative and collisional energy losses.

Evidence is accumulating that products of exothermic reactions are occasionally formed in very high vibrational states. A new case has been reported this year. The flash photolysis of ozone produced vibrationally excited oxygen, probably via the reaction, $O + O_3 \rightarrow O_2^* + O_2$, with the excited oxygen retaining 50 to 60 of the 93 kcal. released [McGrath & Norrish (17)]. This excited species was observed only when a large amount of inert gas was present. Otherwise the ozone sample exploded. The authors suggest that the explosions could possibly be maintained by an energy chain involving the following:

$$O_2^* + O_3 \rightarrow 2O_2 + O(^3P)$$
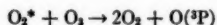
This same system has been analyzed differently by Benson (42) who suggests that a chain reaction involving photon emission and absorption is possible. His mechanism may be applicable to the flash photolysis explosions mentioned above, although an inert gas effect in it is not likely. He postulates the formation of excited oxygen atoms which react to produce the radiator:

$$O_3 + h\nu(3100 \text{ A}^0 \text{ or less}) \rightarrow O_2 + O(^1D)$$
$$O(^1D) + O_2 \rightarrow O_2 + O_2(^3\Sigma_u^-)$$
$$O_2(^3\Sigma_u^-) \rightarrow O_2 + h\nu(2000 \text{ A}^0)$$
$$h\nu(2000 \text{ A}^0) + O_3 \rightarrow O_2 + O(^1D)$$
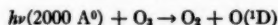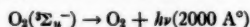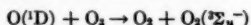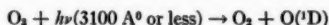
An additional case that requires consideration of energy transfer is the flash oxidation of H_2S [Norrish & Zeelenberg (43)]. When H_2S and O_2 were flashed in the presence of an inert gas, S_2O_2 was formed in a nonexplosive reaction. No light was emitted. When inert gas was not present, SO_2 was formed in an explosion. That the removal of energy by the inert gas is controlling is shown by the fact that the amount needed to repress the explosion is closely related to its heat capacity.

PRIMARY PROCESSES IN ORGANIC REACTIONS

Many organic reactions are radical propagated in the gas phase, and the same radical-molecule reactions occur in several systems. It is helpful, there-

fore, to separate our consideration of these from that of the primary reaction acts.

Many of the latter appear to be either scissions or rearrangements, even in the presence of other reagents. Whether these are induced by quantal absorption of light, collisions with electrically excited atoms, or thermal excitation the conceptual problem is the same. There is some evidence that excited species often are important in each of these types of activation. For example, Manning has pointed out the similarity between the photolytic products and mass spectral fragmentation pattern for aldehyde and ketone photolysis (44). Consequently, the information on primary processes that has accrued from pyrolyses, photolyses, and mercury sensitizations is treated together here. Only a few features of the current work are considered.

A warning is due at this point—most of the statements that follow are deductions from the behavior of complicated systems of sequential and competing reactions. The interpretations often are not exclusive. The difficulties are well illustrated by the many factors that had to be evaluated by Calvert (45) in his analysis of aldehyde and ketone photolysis, the effect of experimental parameters upon quantum yields as recently detailed by Hoare (46), and the general complications attending pyrolysis, many of which are evident in acetylene decomposition [Minkoff, Newitt & Rutledge (47)].

Although a single primary process, usually scission, often has been postulated, there is now a tendency to invoke either a molecular elimination or an atom migration as well in order to explain the quantities of various products observed. Some examples follow. Parsons, Danby & Hinshelwood (48) pyrolyzed ethane and also reacted the products, ethylene and hydrogen, in the presence of large amounts of SF_6, which, acting as a true catalyst, accelerated both reactions. When radical propagated chains are inhibited by the addition of NO, two residual molecular reactions occur:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$
$$\rightarrow CH_4 + [CH_2 \rightarrow \text{products}]$$
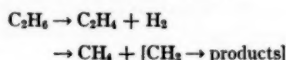
These are accelerated by SF_6, attesting to their unimolecular character.

Trimethylamine photolysis at low temperatures produces H_2, CH_4, ethane, and liquid products [Gesser, Mullhaupt & Griffiths (49)]. These authors suggest that dimethylamine radicals are formed (possibly by decomposition of excited trimethylene molecules), and that the former exhibit the following two modes of decomposition to account for the first two products:

$$(CH_3)_2N \rightarrow H_2 + R$$
$$\rightarrow CH_4 + R$$
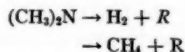
The direct photolysis and radical sensitized decomposition of acetamide occurs via the following reaction:

$$CH_3CONH_2 \rightarrow CH_3 + CONH_2$$
$$\rightarrow CH_3CN + H_2O$$
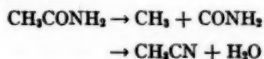
The former is energetically more favorable and is the major reaction, but the latter is indicated by the products [Spall & Steacie (50)].

Mass spectrographic analysis of the free radicals produced in the initial stages of the mercury-sensitized photolytic decomposition of 1,2- and 1,3-butadiene indicate rearrangements occur before scissions [Collin & Lossing (51)].

$$CH_2=C=CH-CH_3 \rightarrow H_2 + C_4H_6$$
$$\rightarrow CH_2-C\equiv CH + CH_3$$
$$CH_2=CH-CH=CH_2 \rightarrow CH_2-C\equiv CH + CH_3$$
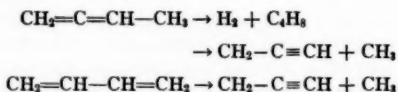
Another case of rearrangement following collisional excitation by mercury may occur in the cracking of ethylene to acetylene and hydrogen. Whalley (52) suggests that the ethylene is excited to a triplet state in which bond distortion is feasible and hydrogen atoms from adjacent carbons can approach each other and then are eliminated as molecular hydrogen.

The initial stage of photolytic decomposition of acetone is well known. At low temperatures the following split occurs, and both radicals react with acetone and themselves: $CH_3-CO-CH_3 \rightarrow CH_3 + CH_3-CO$. At higher temperatures the acetyl radical does not survive but splits to CO and methyl radical. Lossing (53) has examined the mercury-sensitized decomposition using very short (msec.) irradiation with 2537 Å light and continuous sampling of the reaction zone by mass spectrometry. In addition to the initial split into methyl and acetyl, the latter decomposes further to form ketene and H as well as other products. Ketene is not observed in the usual non-sensitized photolysis. In order to explain this, secondary activation by mercury atoms is postulated as follows: $CH_3CO + Hg(^3P) \rightarrow CH_2=C=O + H + Hg$.

Acetaldehyde was treated in the same study, the only primary process found being, $CH_3CHO \rightarrow CH_3 + CHO$, although methane was present in the products. When mixtures of acetaldehyde and CD_3CDO were photolyzed, both CH_3D and CD_3H were found, indicating that the methane was formed by H abstraction.

In his analysis of the photolysis of ketone and aldehyde, Manning (44) shows that the transition of the substrate molecule to an excited state would weaken the carbon-carbon bond adjacent to the carbonyl group sufficiently to permit extensive buckling and rearrangement. This argument leads to the same conclusion as that reached by Kraus & Gilbert (54) who studied the photolysis of butyl and pentyl ketones. The observed distribution of products indicates two primary splits: The usual scission of the C—C bond adjacent to the carbonyl and the breaking of the alpha C—C bond accompanied by a hydride shift from the beta C atom. For example:

$$(CH_3)_2CHCH_2-COCH_2-CH(CH_3)_2 \rightarrow (CH_3)_2CHCH_2 + (CH_3)_2CHCH_2CO$$
$$\rightarrow (CH_3)_2CHCH_2COCH_3 + C_3H_6$$
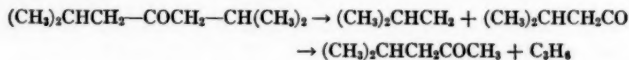
When no H atom was available on the beta carbon atom, as in neopentyl ketone, $((CH_3)_3C-CH_2)_2CO$, the second mode of decomposition did not occur.

Such methods of accounting for major products are not necessarily valid unless evidence pointing to the absence of chain reactions is available. Barry & Walters (55) pyrolyzed methyl n-butyl ketone and found three sets of interrelated major products:

$$CH_3-CO-C_4H_9 \rightarrow C_3H_6 + CH_3COCH_3$$
$$\rightarrow CH_4 + CO + CH_2=CH-C_2H_5$$
$$\rightarrow CH_3COCH=CH_2 + C_2H_6$$
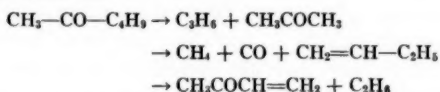
These could possibly be attributed to three different positions of scission accompanied by hydrogen atom migration. However, propylene inhibits the total reaction while not changing the proportions in which CO and the saturated hydrocarbons are produced. Also radical producers such as ethylene oxide, NO (at high temperatures), and biacetyl accelerate the reaction. The last does not disturb the product distribution. Consequently the authors prefer to consider that the major products are formed in sequences involving, first, H-atom abstraction from the parent ketone, then radical decomposition and subsequent repetition of the process; for example

$$R + CH_3COCH_2CH_2C_2H_5 \rightarrow RH + CH_3COCHCH_2C_2H_5$$
$$C_2H_5 + CH_3COCH{:}CH_2 \leftarrow^|$$
$$C_2H_5 + CH_3COCH_2C_2H_5 \rightarrow C_2H_6 \text{ etc.}$$
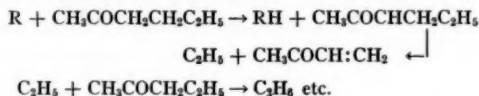
Another case in which the interplay of primary and secondary processes is unclear is that of the photolysis of cycloketones [Blacet & Miller (56)]. Cyclohexanone, pentanone, and butanone were photolyzed at three wavelengths: 2537, 2654, and 3130 A and at 100 to 300°C. At the two shorter wave lengths the quantum yields were temperature independent. CO was a principal product, and the cycloparaffin resulting from CO elimination was obtained in moderate yield in all cases. Straight chain olefins were present in small amounts except for pentene-1 which was formed from cyclohexanone in moderate yield. In terms of the scissions discussed for the butyl ketones, both straight chain methyl ketones and the $(n-1)$ olefins would be expected in moderate amounts. If the cycloparaffin is not formed by internal rearrangement before the elimination of CO, the chances of H atom abstraction by radicals would be high. It would be interesting to know the behavior of these systems in the presence of a substrate such as C_2D_6.

Ketene photolysis has been studied extensively. When reaction occurs, the only type of primary process seems to be the elimination of CO with the resultant formation of a diradical of an extremely reactive type (57–60):

$$R=C=O \rightarrow CO + R=$$
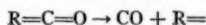
This may occur immediately upon absorption of light at short wavelengths, but at longer wavelengths, viz., 3650 A, an excited ketene molecule is the initial product. Porter (61, 62) photolyzed ketene at low pressures and also in the presence of oxygen. The quantum yield of CO at low pressures is less than 1 (also true at higher pressures), indicating that initially excited

ketene molecules lose their energy by collisions. Low concentrations of oxygen produce the same effect—the main interaction of ketene and oxygen being deactivation of the latter rather than reaction.

When oxygen and ketene do react (excitation at 3650 A) the CO yield parallels the oxygen consumption. Very little ethylene is formed. Shorter wavelength excitation (2700 A) leads to appreciable ethylene even in the presence of oxygen. These facts are interpreted as an interaction of oxygen and excited ketene rather than methylene. The puzzling feature of the system is not the excited molecule reaction but the efficient ethylene production at shorter wavelengths where a reaction with a triplet oxygen molecule is possible.

BIMOLECULAR REACTIONS

A few metathetical reactions of atoms and radicals have been mentioned above in connection with other topics. A number of examples, principally concerned with atom transfers in organic systems, are considered here.

Sodium atoms.—A reanalysis of the behavior of low pressure diffusion flames has enabled Reed & Rabinovitch (63) to improve the method and examine the reactions of sodium vapor with the fluorochloromethanes. In each case a Cl atom is abstracted first but then reactions occur between the remaining radical and Na. For example, the reaction with CF_3Cl produced the following products in the relative amounts indicated: C_2F_6 (1), C_2F_4 (0.74), C_4F_8 (trace) and carbon. The salt deposit contained NaF: NaCl = 0.75. The secondary reactions were less pronounced in other cases. Activation energies were estimated, assuming unit steric factors, for the primary abstractions of Cl: $CH_3Cl = 9.8$, $CFH_2Cl = 10.1$, $CF_2HCl = 10.0$, and CF_3Cl = 9.2 kcal./mole. Comparison of this last value with an earlier value, 6.2 kcal. (64), suggests a systematic error. This probably is due to the reinterpretation of the method. The recent results are likely to be correct. Definite values for rate constants for the secondary reactions were not obtained but estimates were made of the lower limits for k's for abstraction from the fluorinated methyl radicals. They all are within a factor of 10 of the rate for $2CF_3 \rightarrow C_2F_6$ which was taken as $k = 2 \times 10^{13}$ cc./mole·sec.

Chlorination.—The chlorination of ethylene and ethane derivatives has been investigated extensively. An extensive study of the photochlorination of C_2Cl_4 and C_2HCl_5 provides the rates of individual reactions [Ackerman *et al.* (65)]. Four self-consistent rate constant ratios were determined from nine separate types of experiments. Earlier reports were discussed here last year (22). The mechanism used to explain chlorination in a mixture of the two substrates is as follows:

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + C_2Cl_4 \underset{4}{\overset{2}{\rightleftarrows}} C_2Cl_5$$

$$Cl + C_2HCl_5 \underset{4'}{\overset{2'}{\rightleftarrows}} C_2Cl_5 + HCl$$

$$C_2Cl_5 + Cl_2 \underset{5}{\overset{3}{\rightleftarrows}} C_2Cl_6 + Cl$$

$$2Cl + M \overset{6}{\rightarrow} Cl_2 + M$$

$$C_2Cl_5 + Cl \overset{7}{\rightarrow} C_2Cl_6$$

$$2Cl_2Cl_5 \overset{8}{\rightarrow} C_4Cl_{10}$$
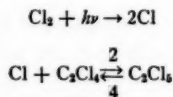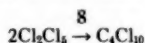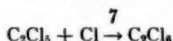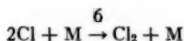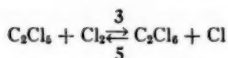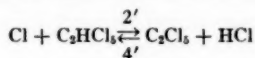
The rate ratios obtained were k_2/k_2', k_3/k_4, $k_3/(k_8)^{1/2}$, and $(k_3k_2'/k_7)^{1/2}$. The corresponding activation energy differences reported are $E_2'^* - E_2^* = 5.22$ kcal./mole, $E_4^* - E_3^* = 16.24$, $E_3^* - E_8^*/_2 = 3.02$, and $E_3^* + E_2'^* - E_7^* = 6.17$.

A closely related case is the chlorination of trichloroethylene [Dainton, Lomax & Weston (66)]. A similar mechanism applies and presumably steps such as reaction $2'$ (above) occur but are unimportant.

$$Cl_2 + h\nu \rightarrow 2Cl$$

$$Cl + C_2HCl_3 \overset{10}{\rightarrow} C_2HCl_4$$

$$C_2HCl_4 + Cl_2 \overset{11}{\rightarrow} C_2HCl_5 + Cl, \; E_{11}^* = 5.1 \text{ kcal./mole}$$

$$2C_2HCl_4 \overset{12}{\rightarrow} \text{inactive products}, \; E_{12}^* = 0.5 \text{ kcal./mole}$$
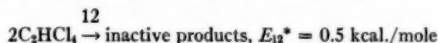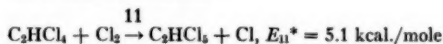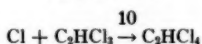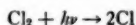
In a correlation of these systems, E_{11}^* should parallel E_3^*, and E_{12}^*, E_8^*. This leads to a value for E_4^* close to that previously reported (21 kcal.). Then either reaction 2 or 7 is required to have a negative temperature coefficient of the order of $E^* = -2$ kcal./mole. In view of the recombination studies, on bromine atoms (above), this may be allowable, although radical recombination results cast doubt on the negative value.

The thermal decomposition of chloroform shows many of these molecules as products, and probably many of these elementary reactions are applicable [Semeluk & Bernstein (67)]. An appreciable H,D isotope effect was observed, $k_h/k_d = 1.20$ for the experimental temperature range (450 to 525°C.). As pointed out by the authors this is undoubtedly a composite of the effects for the various steps. Photo-chlorination experiments might assist in pinpointing the isotope dependent reactions while avoiding the reactions of chlorinated ethanes and methanes that occur at pyrolysis temperatures.

ORGANIC FREE RADICALS

Extensive study of methyl radical reactions for a number of years has established the main features. As a result, CH_3 has become a tool for the investigation of other reactions. This does not mean that the quantitative information about abstraction reactions of CH_3 is all well established. A case

in point is discussed by Long (68) who considers the two reported values of the activation energy for the following:

$$CH_3 + H_2 \rightarrow CH_4 + H, \text{ from which } E^* = 9.7 \text{ or } 13 \text{ kcal./mole.}$$
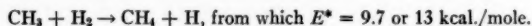
He concludes that the lower value is in error. It depended upon comparison of CH_4 production with the ethane formed in the reaction $CH_3+CH_3 \rightarrow C_2H_6$. A significant amount of ethane can be lost by further attack $[CH_3+C_2H_6 \rightarrow CH_4+C_2H_5]$ and the subsequent formation of polymer. The higher value is based upon the CH_4/CH_3D ratio in the competitive abstraction from HD or D_2, H_2 mixtures. The ethane problem being experimentally less acute here, the author favors the high value.

Radical exchange, rather than abstraction, can occur in some systems. Pritchard & Steacie (69) produced methyl radicals from azomethane in the presence of hexafluoroacetone. CF_3H and CF_3CH_3 were found in small amounts. Since CO was not a product, the readily decomposable CF_3CO radical was probably not an intermediate ruling-out process such as the following:

$$CH_3 + (CF_3)_2CO \rightarrow CH_3CF_3 + CF_3CO$$

$$CF_3CO \rightarrow CF_3 + CO$$
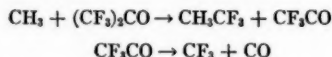
The authors evaluated the system in terms of the following reaction sequence and established $E^* = 6$ kcal./mole:

$$CH_3 + (CF_3)_2CO \rightleftharpoons [(CF_3)_2COCH_3] \rightarrow CF_3COCH_3 + CF_3$$

The use of methyls as tools is well illustrated in several papers. Landers & Volman (70) initiated polymerization of acetylene, butadiene, ethylene, and propylene with methyl radicals. Their results are consistent with earlier work in the field. Their main interest was in the kinetics of propagation of the growing polymer chain. Activation energies for polymerization of these four substrates were, respectively, 5.1, 4.9, 8.2, and 5.6 kcal./mole. These represent the energetic barrier for the addition of a generalized hydrocarbon radical to the various double bonds.

The high value of the activation energy for the addition to ethylene is the major difference between this and previous polymerization studies. An independent estimate of this process is available from the recent study of Pinder & Le Roy (71). They evaluated the relative amounts of butane and hexane formed in the mercury sensitized photolysis of hydrogen with ethylene present. Arguing that the major source of butane is

$$2C_2H_5 \rightarrow C_4H_{10} \qquad\qquad k_1$$
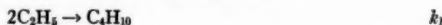
and that hexane is formed by

$$C_2H_5 + C_2H_4 \rightarrow C_4H_9 \qquad\qquad k_2$$

$$C_4H_9 + C_2H_5 \rightarrow C_6H_{14}$$
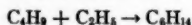
the activation energy for reaction 2 was found to be 5.5 kcal./mole. The ratio of $k_2/(k_1)^{1/2}$ for ethyls is about one-fifth that for the ratio of methyl

addition to ethylene relative to methyl recombination. Long's criticism of the methyl-hydrogen reaction may apply here, in which case the observed butane would be somewhat increased by abstraction of H by C_4H_9 and the experimental activation energy would be lowered.

McNesby & Gordon (72) have extended the application of their techniques employing deuterated acetone to a study of the effect of ring size upon abstraction reaction parameters. The principal abstraction reactions possible for CD_3, produced from hexadeutero acetone are:

$$CD_3 + CD_3COCD_3 \rightarrow CD_4 + CD_2COCD_3$$

$$CD_3 + RH \rightarrow CD_3H + R \qquad\qquad k_2$$

By analysis of the CD_3H and CD_4 yields the abstraction activation energies in kcal. per mole were determined for cyclopropane and cyclopentane, $E_2^* = 13.1$ and 9.3, respectively. These are similar to the results for abstraction from paraffins. The radical intermediates in the first system, cyclopropyl and allyl, did not catalyze the isomerization of cyclopropane to propylene. This provides more, indirect, support for the unimolecular nature of that process.

In the case of cyclopentane, hydrogen was formed as well as ethane, propylene, and ethylene. Since the ring was stable at the temperature of the experiments, the authors suggested that the organic products were formed by various decompositions of the radical formed upon ring fracture. This was substantiated by pyrolysis of cyclopentane (515°C.) both in the presence of D_2 and deutero-acetone (73). Unlabeled ethylene and propylene were the major products. Only traces of C_2H_5D appeared while 10 to 15 per cent of the propylene was C_3H_5D. This product distribution may either be attributed to a unimolecular decomposition or to the chain:

$$C_5H_{10} \rightarrow C_5H_9 + H$$

$$C_5H_9 \rightarrow CH_2CH_2CH_2CH{=}CH_2 \rightarrow CH_2{-}CH{-}CH_2 + C_2H_4$$

$$CH_2{-}CH{-}CH_2 + D_2 \rightarrow C_3H_5D + D$$

$$CH_2{-}CH{-}CH_2 + C_5H_{10} \rightarrow C_5H_9 + C_3H_6$$
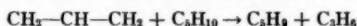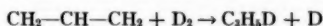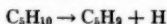
The yield of hydrogen was not, however, based upon the initiation step in this chain. Analysis of the HD/H_2 ratio in experiments in which deuteroacetone was photolyzed to initiate the reaction showed very little isotopic mixing. An intramolecular elimination of H_2 from the cyclopentyl radical to form a long-lived resonance stabilized cyclopentenyl radical appears probable.

These same experiments offered an opportunity for study of the abstraction reactions of allyl. Even at high temperatures it is less effective than methyl. The authors suggest that the stability of allyl accounts for the commonly observed inhibitory effect of propylene. This molecule serves as a substrate for H abstraction, producing the stable allyl which does not react readily to continue the chain reaction.

The reactions of CD_3, with butenes are revealing [McNesby & Gordon

(74)]. H abstraction occurs from the alpha carbon, forming CD_3H. In addition CH_4 and CH_3D appear. These products correlate with the amounts of deuterated butenes, etc. found in the products, and indicate a methyl exchange analogous to that mentioned above for hexafluoroacetone:

$$CD_3 + CH_2{=}CH{-}CH_2{-}CH_3 \rightarrow CD_3H + CH_2{=}CH{-}CH{-}CH_3$$
$$\rightarrow [CD_3CH_2CHCH_2CH_3] \rightarrow CD_3CH_2CH{=}CH_2 + CH_3$$
$$\rightarrow [CH_3{-}CH(CD_3){-}CH_2CH_3] \rightarrow CH_2{=}CH{-}CD_3 + CH_2CH_3$$
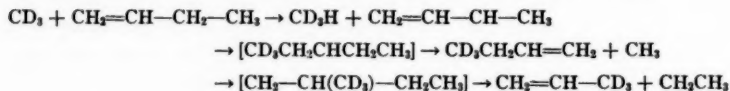
It would appear that such exchanges must be considered in other methyl radical systems. Certainly this work shows that detailed product analysis is well worth the effort. It also suggests that radiocarbon labeling of substrates should be employed more frequently (as well as D-labeling) in order to point out the group scrambling.

The elaboration of the behavior of the diradicals produced from ketenes has received much attention. Normally the dominant reaction is rapid attack of the parent compound as follows:

$$CH_2{=}C{=}O \rightarrow CH_2 + CO$$
$$CH_2 + CH_2{=}C{=}O \rightarrow CH_2{=}CH_2 + CO$$
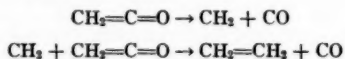
This is demonstrated by the fact that at $-78°C$. a quantum yield of 2 may be achieved for CO production (60) and by the very rapid formation of ethylene observed by Kistiakowsky & Kydd (57). They coupled a time of flight mass spectrometer with flash photolysis in order to analyze the reaction products as soon as 100 μsec. after irradiation. In this time ethylene formation was complete.

Ethylidine, ($CH_3CH{=}$), formed from methyl ketene photolysis [Kistiakowsky & Mahan (58)] has two options. Some ethylene is formed, but it decreases relative to the CO yield as the energy of the exciting quantum is decreased and as inert gas is added to the system. The authors postulate that ethylidine produced in a high energy state can rearrange to ethylene before it reacts, but that a cold radical undergoes the normal reaction forming butane. Finally, photolysis of ketene in the presence of excess ethylene (75) offers further evidence that CH_2 reacts easily as a diradical. Using 3100 A radiation and a ratio of 7.5:1 for ethylene:ketene, the quantum yield of cyclopropane was always appreciable, and, at high pressures, reached a limiting value of 0.6.

For a moment we may turn from this welter of atom transfer and addition reactions to consider electron transfer and ion-molecule additions. Many charge transfer reactions have rates comparable to the collision number [Stevenson (76)]. Ion-molecule addition reactions may either form stable ions (buildup of heavy "fragments" in mass spectra) or metastable ions that then decompose to their characteristic fragmentation patterns. A collision theory of ion-molecule reactions has been advanced by Field, Franklin & Lampe (77, 78) who studied the reactions of methane, acetylene, and ethylene with their ions. The rates of these reactions are all high, cor-

responding to reaction cross-sections somewhat greater than normal molecular dimensions.

Auto-oxidation.—Oxidation by molecular oxygen remains a major problem mechanistically because of the large number of intermediates and products. Valuable work is still being done on the identification of products, and few contributions have been made this year on the rates of individual steps. Once the parent molecule has been attacked and a radical is formed, there is general agreement that oxygen reacts rapidly, probably without activation energy, with the radical to form some peroxy species. Hoare & Walsh (79) consider that these are trimolecular processes and, from acetone photolysis in the presence of oxygen, evaluate the rate of the reaction,

$$M + CH_3 + O_2 \rightarrow M + CH_3OO, \qquad\qquad k_1$$
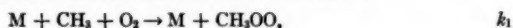
as $k_1 = 1.6 \times 10^{-31}$ (cm.^{3}/molecule)^2 sec.$^{-1}$ Similar rates result for methyls produced from azomethane and from dimethyl mercury. A photolytic study of diethyl ketone and oxygen [Jolley (80)] showed that the production of CO was reduced by the presence of oxygen. This was interpreted as a reaction of the propionyl radical with O_2:

$$CH_3CH_2CO \rightarrow CO + C_2H_5 \qquad\qquad k_2$$

$$CH_3CH_2CO + O_2 \rightarrow CO_2 + C_2H_5O \qquad\qquad k_3$$

For these, $E_2{}^* - E_3{}^* = 13$ kcal./mole, and the steric factor ratio $A_2/A_3 = 10^3$.

When a low temperature ($<200°C.$) oxidation of ethane is initiated by a mercury sensitized process apparently the excited mercury can start two types of chains [Watson & Darwent (81)]. Energy may be transferred to the organic substrate, with subsequent dissociation, or to oxygen, which may either add to the substrate or abstract hydrogen:

$$Hg(^3P) + C_2H_6 \rightarrow Hg + C_2H_5 + H$$

$$Hg(^3P) + O_2 \rightarrow Hg + O_2{}^*$$

$$C_2H_6 + O_2{}^* \rightarrow C_2H_5OOH$$

$$\rightarrow C_2H_5 + HO_2$$

$$\rightarrow C_2H_5OO + H$$
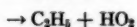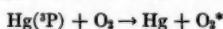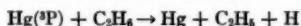
The main product was ethyl peroxide with a quantum yield near unity. There was little indication of an extended chain reaction, i.e., of abstraction of H from ethane by ethylperoxy radicals at these temperatures.

Other reactions.—Although apparently preoccupied with the reactions of organic entities, kineticists have not cast aside their first loves. Benson & Axworthy (82) confirmed Schumacher's data on ozone decomposition and successfully interpreted the decomposition of both dilute and concentrated ozone on the basis of the Jahn mechanism

$$M + O_3 \rightarrow O_2 + O + M$$

$$O + O_3 \rightarrow 2O_2$$
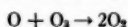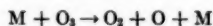
Kistiakowski & Volpi (83) and Ford & Endow (84) have evaluated atom

reactions with nitrogen oxides using stirred reactors and mass spectrometric and photometric techniques respectively. Specific rates found were as follows:

$$N + O_2 \rightarrow NO + O \quad k = 2 \times 10^{12} \exp(-6.20/RT)$$

$$O + NO_2 + M \rightarrow NO_3 + M \quad k = 1 \times 10^{17} \text{ (cm}^3./\text{mole)}^2 \text{ sec.}^{-1}$$

$$O + NO_2 \rightarrow NO + O_2 \quad k = 2.1 \times 10^{12} \text{ cm}^3./\text{mole. sec. (room temperature)}$$

$$O + NO + M \rightarrow NO_2 + M \quad k = 1.8 \times 10^{16} \text{ (cm.}^3/\text{mole)}^2 \text{ sec.}^{-1}$$
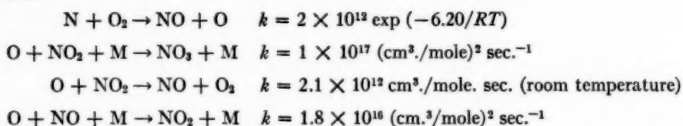
In addition, the former authors placed bounds upon the rates of several related reactions. Ray & Ogg (85), using the reaction $NO_2 + NOCl \rightarrow NO + NO_2Cl$ to produce trace amounts of NO, followed the reaction $NO_2 + O_2 + NO \rightarrow NO_2 + NO_3$, and found $k = 6.6 \times 10^7$ (cc./mole)^2 sec.$^{-1}$ at room temperature. This rate constant, combined with the extensive data on N_2O_5 decomposition, permitted a calculation of the entropy of formation of N_2O_5. Agreement with statistical mechanical calculations was obtained.

The high temperature oxidation of hydrogen by both NO [Graven (86)] and NO_2 are reported [Rosser & Wise (87) and Ashmore & Leavitt (88)]. Both are chain reactions propagated by OH radicals and are sensitive to wall effects. The apparent activation energies are similar (41, 43 to 46 kcal./mole, respectively). The initial rate of oxidation of ammonia at 600 to 800°C. by NO_2 [Rosser & Wise (89)] is first order in each; $E^* = 27.5$ kcal./mole, and the products are N_2 and NO, with the former enhanced by the addition of NO. The authors explain this in terms of a reaction of NO with the intermediate NH_2 eventually yielding N_2.

Hydrogen peroxide, concentrated and freed from catalytic impurites, decomposes homogeneously in a first order process (initially) above 400°C., and $k = 10^{13} \exp(-48.0/RT)$. D_2O_2 decomposes at the same rate, indicating that O—O bond cleavage is rate controlling [Giguere & Liu (90)]. In another study, peroxide was decomposed in the presence of excess water vapor. The reaction was 3/2 order, $E^* = 55.0$ kcal./mole, and long chains were indicated [Satterfield & Stein (91)]. The agreement is good. The two studies emphasize different features of a complex system.

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REACTION KINETICS IN SOLUTION[1]

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This review is somewhat more restricted than it has usually been in the past. A number of topics such as polymerization, enzyme kinetics, and photochemistry are not treated, and in the field of organic reactions only a limited number of reaction types is included. Also, the subjects specifically treated here suffer some limitation imposed by the unavailability of a number of journals. For these, the reviewer has relied upon secondary sources such as *Chemical Abstracts* and *Chemisches Zentralblatt.*

Mathematical technique and treatment of data.—Alberty & Miller (1) have given integrated rate equations for isotopic exchange reactions accompanied by a reversible chemical change, including the cases where isotope effects are present both in the exchange and in the chemical reaction. Giacometti & Iliceto (2) have treated the case of an isotopic exchange reaction in which one of the reactants undergoes an irreversible first-order change, the products of which are unable to undergo further exchange. The case of a first-order reversible reaction with isotopic exchange between reactant and product is treated by Guerreschi (3). Noyes (4) has developed rate expressions for the special case of competition between a time-independent unimolecular process and a time-dependent bimolecular one, a situation which arises in the quenching of fluorescence. Hirschfelder (5) considers the mathematics of the pseudostationary state approximation and devises a method for testing its validity in specific examples. Higghins (6) has derived, and applied, rate equations for reactions between unifunctional molecules and molecules which are unifunctional at one position and n-functional at another. Talat-Erben (7) examines the maximum amount of the intermediate formed in uni-bi, bi-uni, and bi-bimolecular consecutive reactions, as a function of temperature and initial concentration. A simplified method for obtaining order and rate constant for reactions in which the rate is proportional to powers of the concentration of a single reactant is presented by Chang (8), Flynn (9) describes a graphical method that may be useful to fit complex reactions in a rate equation, and Rastogi (10) derives rate expressions for a number of complex reactions in a flow system. McMillan (11) develops an equation for obtaining the ratio of the rate constants for two competitive consecutive second-order reactions.

The absorption and dispersion of sound resulting from a chemical equilibrium in a liquid is discussed by Tabuchi (12) and also by Maier &

Rudolph (13), who show how the rate constants may be obtained from acoustic data; the latter authors apply the method to the measurement of rate of association and dissociation of hydrogen-bonded molecules (14).

Fast reactions.—By combining equilibrium constants with rate data for the reaction of ethyl iodomalonate with iodide ions, Bell & Engel (15) have deduced the rate for the very fast reactions of iodine and tri-iodide ion with enol and enolate ion; the rate constants are close to the collision number. The recombination rate of iodine atoms in solution has been measured by Willard by means of flash photolysis technique, in which the value of the activation energy suggests a diffusion controlled process (16). The bimolecular rate constants for the electron exchange between naphthalene negative ions and naphthalene are measured by means of electron magnetic resonance method by Ward & Weissman (17) and found to vary in the range 10^7–10^9 $1.mole^{-1}$ sec.$^{-1}$, according to the nature of the solvent and cation. Nuclear magnetic resonance spectroscopy may also be used to evaluate the rate of very fast electron transfers; significant papers in this field have appeared by McConnell *et al.* (18). By means of a flow method, Meier & Schwarzenbach (19) measure the rate of dehydration of carbonic acid and find that the reaction is not simply first order. At the higher H_2CO_3 concentrations there is a contribution from a quadratic term, which is believed to arise from the reaction, $2 H_2CO_3 \rightarrow HCO_3^- + H_3CO_3^+$, followed by the fast decomposition of $H_3CO_3^+$.

Pressure effects.—The Faraday Society has published a discussion on the physical chemistry of processes at high pressures, a large part of which is devoted to kinetics in solution. Hamann & Teplitzky (20) report the pressure effects on the addition of halogens to olefins, and on the Menschutkin reaction; Norrish & Nicholson (21) and Ewald (22) give data on free radical dissociations, while Weale (23) discusses the possible effects of pressure on steric hindrance. Norrish & Nicholson (24) and Laird *et al.* (25) study polymerization kinetics at high pressures, and Laidler (26) treats the solvent effects and the correlation between volumes and entropies of activation as revealed by high-pressure studies. Other high-pressure kinetic studies are those of Walling & Pellon (27) on the decomposition of benzoyl peroxide and the polymerization of styrene and allyl acetate, and of Hamann *et al.* (28) on the iodine-catalyzed *cis-trans* isomerization of 1,2-dichloroethylene.

MEDIUM EFFECTS

Winstein and his collaborators (29) have continued to investigate the applicability of the equation log $(k/k_o) = mY$ to the correlation of solvolysis rates, extending their studies to a great variety of solvent mixtures for which the Y values are now available, and to structurally different substrates. Their results bring to light the severe limitations which affect the above relationship in the form in which it had originally been conceived: the adoption of a single m value for a given compound leads to great dispersion, while a very good fit is obtained for any given solvent pair. It is then appar-

ent that the parameter m is not a characteristic solely of the substrate, but also of the solvent pair; within these limits the mY relationship may be very profitably used for interpolative purposes. The work also includes a thorough comparative discussion of Winstein's and Swain's correlations.

Swain's "push-pull" termolecular mechanism of solvolytic reactions (30) has been strongly criticized by Hughes and his co-workers (31), who have reinvestigated the kinetics of the reactions of triphenylmethyl chloride in benzene with tetralkylammonium chloride and azide, and with polar molecules such as alcohols. They have obtained many results which contrast with those found previously by Swain for the same systems; consequently, they consider Swain's deductions and generalizations as completely unjustified. To quote just one example: in the reaction with tetrabutylammonium chloride, the rate is greatly enhanced by added polar molecules such as nitromethane or alcohols; however, contrary to Swain's findings, such addenda do not display a definite kinetic order but, if the concentration range is sufficiently extended, the "order" steadily increases with concentration, in some cases from zero up to three, Therefore, it is not justified to assign to such molecules a definite role and position in the transition state, rather "the number and position of these catalyst molecules . . . are . . . capable of correct description only in the statistical terms appropriate to macroscopic cosolvent effects." The mechanistic scheme suggested to replace Swain's, is a modified S_N1 mechanism in which two slow steps are involved. For instance, in the reaction of triphenylmethyl chloride with the salt, MX leading to the substitution of X for Cl, the following sequence is found:

$$
\begin{array}{ccccc}
(a) & (b) & & (c) & \\
\text{slow} & \text{fast} & & \text{slow} & \text{fast} \quad \text{fast} \\
\text{RCl} \underset{\text{fast}}{\overset{\text{slow}}{\rightleftarrows}} \text{R}^+\text{Cl}^- \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} (\text{R}^+\text{Cl}^-)(\text{M}^+\text{X}^-) \underset{\text{slow}}{\overset{\text{slow}}{\rightleftarrows}} (\text{R}^+\text{X}^-)(\text{M}^+\text{Cl}^-) \underset{\text{fast}}{\overset{\text{fast}}{\rightleftarrows}} \text{R}^+\text{X}^- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftarrows}} \text{RX}.
\end{array}
$$
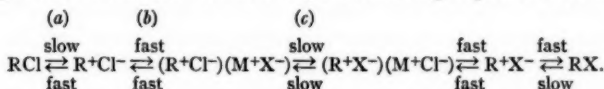
Step (a) is the slow ionization of RCl, which is followed by the rapid dipole association (b); the second slow step is the quadrupole rearrangement (c). Some theoretical justification for the energetics of the steps involved is also given. These ideas are also discussed by Ingold in a lecture on polar reactions in nonpolar media (32). Poker (33) also describes the catalysis of hydroxy compounds and salts in the displacement of methyl bromide with pyridine in benzene, in terms of macroscopic cosolvent effects.

In order to explain the invariance of rate with dielectric constant in the Np(V)-Np(VI) exchange, Amis (34) suggests that the reactant ions are preferentially solvated with the higher dielectric component of the solvent mixture; the activated complex is supposed to consist of a bridge arrangement of some kind, incapsulated by successive, dielectrically saturated, solvation shells which contain the more polar component only. The same author has measured rate and activation parameters for the hydrolysis of ethyl acetate, as a function of solvent composition (35), and LeRoux (36) discusses the solvent effect on ion-dipole reactions. The solvolysis rates of a tertiary halide in the two nonproduct-forming solvents, dimethylformamide

and N-methylpropionamide (dielectric constants 37 and 164, respectively) differ but little [Ross & Labes (37)]. Miller and his co-workers studied the alkaline hydrolysis of esters in water-dioxane mixtures which contain a third component such as alcohols, acetone, and lactamide (38), and Sadek & Abu Elamayen (39) investigated the influence of polyvalent alcohols. The resulting effects are discussed in terms of specific solvation of reactants and transition states.

Solvent effects in radical reactions have been noted. Russell (40) finds that the relative reactivity of chloride atoms toward primary and tertiary hydrogen atoms is greatly altered in the presence of aromatic solvents; thus, the ratio ter-chloride/prim-chloride increases with increasing concentration of the aromatic component and varies with the nature of the aromatic. Walling & Miller (41) also observe that the relative reactivities of toluenes toward chlorine atoms vary from carbon tetrachloride to benzene solvents; both authors suggest that formation, between aromatics and chlorine atoms, of π-complexes having greater selectivity than free chlorine atoms, and Russell points out that these findings call for a reappraisal of many homolytic substitutions, particularly those involving competition reactions.

The decomposition of 4-methoxy-3',5'-dinitrobenzoylperoxide is subject to general acid catalysis and is accelerated by polar solvents. This finding and the pattern of products in different media suggest that a shift from a radical to a nonradical mechanism obtains in the more polar solvents. [Leffler (42)]. Schwartz (43) studied the solvent effect on the rate of dissociation of aliphatic nitroso dimers.

A number of papers deal with the effect of neutral salts. Worthy of mention here are the works of Carassiti & Dejak (44), Reinheimer *et al.* (45), and Eaborn & Parker (46). Remarkably close agreement between theory and experiment is found by the latter authors for a reaction between two univalent negative ions, up to ionic strengths of 1.0.

ISOTOPE EFFECTS

Kinetic isotope effects have been extensively investigated which is not surprising if one considers the kind of detailed mechanistic information which the method may offer. In this section, a number of such studies are recorded, and more are referred to under specific reaction types. Exact equations for calculating experimental isotope effects have been derived by Tong & Yankwich (47) who also discuss in detail the various cases in which their equation may be profitably used.

Secondary hydrogen isotope effects have been measured by Saunders *et al.* in the solvolysis of deuterated 2-phenylethyl tosylate (48), and by Shiner and his colleagues in the solvolysis of p-deuteroalkyl benzhydryl chlorides and of α-deuteroketals (49, 50). The magnitude of the effect depends upon the nature of the substituents on the α-carbon and on the polarity of the solvent medium. These secondary effects are commonly taken as a measure of the hyperconjugative stabilization of the transition state. Swain,

however, disagrees with this view (51), and Halevi (52) advises that, before drawing any conclusion as to their mechanistic significance, the possibility should be considered that C—D and C—H bonds may differ in their ground state inductive effects.

The absence of a kinetic isotope effect in electrophilic aromatic substitutions is generally accepted as evidence for the fact that the C—H bond is not appreciably affected in the slow step, which presumably leads to the formation of an intermediate. Thus, De la Mare and his co-workers (53) find no appreciable rate difference in the bromination of benzene and hexadeuterobenzene. Grovenstein & Kilby (54) on the other hand , find $k_H/k_D = 4$ in the iodination of 2,4,6-trideuterophenol. This result by no means disproves the formation of an intermediate; rather, it may be interpreted by the assumption that the slow step is the decomposition rather than the formation of an intermediate. Other relevant papers in this area are those of Berglund-Larsson (55) and Halvarson & Melander (56).

The rate effects obtained upon substitution of D_2O for H_2O in the solvent medium have been measured by several authors. Duncan & Lynn (57) find $k_D/k_H \simeq 2$ in the pinacol-pinacolone rearrangement, while $k_D/k_H \simeq 4$ is found by Ingold *et al.* in the benzidine rearrangement. This unusually large effect supports the view that the second conjugate acid of hydrazobenzene is involved in the slow step (58). On the other hand, practically no effect is obtained in the oxidation of Pu(III) by oxygen, which suggests that no transfer of hydrogen occurs in the rate step [Baker & Newton (59)]. In the hydrolysis of methyl- and phenylmagnesium bromide in tritiated water, k_H/k_T is of the order of 2 [Assarsson (60)].

In the reduction of triphenylmethyl cations by deuterated formic acid, k_H/k_D ranges from 2.5 to 4.9, suggesting a hydride transfer from formate ion [Stewart (61)]. The identical hydrogen isotope effects which are obtained both for bromination and hydrolysis of 1-chloronitroethane show that both reactions proceed by way of a common intermediate, probably the tautomeric *aci-* form [Hawthorne & Strahm (62)]. Hodnett & Flynn found that in the decomposition of p-nitrophenyl-β-t_1-trimethylammonium iodide in water, the β-hydrogen is removed 7.4 times faster than the tritium atom (63). Russell (64) observed that in the auto-oxidation of aralkyl hydrocarbons, the k_H/k_D ratios are 5.5 and 1.9 for the propagation and termination steps, respectively.

Daniels & Magee demonstrated that in the decomposition of substituted ureas the C^{13} isotope effect depends upon the nature of the substituents and rationalize the results in terms of resonance interactions at the transition state (65). A temperature dependence of the C^{14} isotope effect is noted by Duncan & Lynn in the pinacol-pinacolone rearrangement (66), and Bender & Holg (67) found that the C^{14} isotope effect in the direct displacement of methyl iodide with triethylamine in benzene is of the same order as for reactions involving complete bond rupture. Consequently, the criterion cannot be used to distinguish between uni- and bimolecular displacements.

A lecture demonstration proposed by Zollinger (68) should prove useful to the teacher who wants to emphasize the importance of isotopic effects in mechanistic studies.

Inorganic Reactions

Electron transfer reactions.—Many papers in this field discuss the nature and role of bridging groups in the charge transfer process. Sullivan *et al.* (69) studied the reversible reaction, $Np(IV) + Np(VI) \rightleftarrows 2Np(V)$, and find that in sulfate media both forward and reverse reactions involve several parallel paths. Sulfate groups participate in the transition state, although they probably do not function as bridging ligands, this role rather being played by hydroxyl groups. The same authors (70) have studied the isotopic exchange between Np(V) and Np(VI) and find, $Rate/[Np(V)][Np(VI)] = k_1 + k_2[H^+]$. The magnitude and direction of the rate effects which obtain upon substitution of D_2O for H_2O imply the deduction of the mechanisms of charge transfer; for the acid-independent path this is visualized as occurring through a water bridge without group transfer, while for the acid-dependent path a hydrogen-atom transfer is indicated. The question as to whether H_2O and OH^- can function as bridging ligands in electron transfer reactions involving aquo cations has been considered by Taube *et al.* (71) who have investigated the reduction of cobaltpentaminoaquo cation by Cr^{++}. The reaction seems to occur by way of two independent paths involving $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_5OH]^{++}$, respectively. Tracer experiments show that, in the latter path, practically complete transfer of oxygen takes place, and isotope fractionation data support the view that in the activation process both Co—O and Co—N bonds are considerably stretched.

Brubaker and his co-workers (72) have extended the study of the Tl(III)-Tl(I) exchange to sulfate media, in which the rate is about 200 times faster than in perchlorate. The operation of the sulfate ions is viewed as not simply that of decreasing the charge of the reacting entities, but rather as that of bridging groups; in presence of chloride, effects are obtained which are very similar to those previously discovered by Dodson (73).

The kinetics of the Hg(I) oxidation by Tl(III) follow the expression, $Rate = k'[Hg(I)][Tl(III)]/[Hg(II)]$; the slow step appears to be a two-electron transfer between the species $TlOH^{++}$ and Hg (the latter arising from the reversible dismutation of Hg_2^{++}). The specific rate for the process is estimated to be about 10^9 times higher than for the analogous two-electron transfer between $TlOH^{++}$ and Tl^+. This comparison is interesting since the species Tl^+ and Hg are isoelectronic, differing only in their charge. The results show that the large rate difference arises essentially from the difference of the entropy terms [Armstrong & Halpern (74)]. Irvine (75) finds the following expression for the reduction of Tl(III) by trisdipyridylosmium (II) in aqueous perchloric acid: $Rate/[Os(II)][Tl(III)] = k_a[H^+] + k_bK/(K+[H^+])$, where k_a and k_b are the specific rates for the reaction of Os(II) complex with Tl^{3+} and $TlOH^{++}$, respectively, and K is the first hydrolysis constant of Tl^{3+}.

In aqueous perchloric acid the Pu(III)-Pu(IV) exchange is expressed by, Rate/$[Pu^{3+}] = k_1[Pu^{3+}] + k_2[PuOH^{3+}]$; the activation energies for the two processes are 7.7. and 2.8 kcal. [Keenan (76)]. For the Fe(III)-Fe(II) exchange in the presence of SCN^- ions, two reaction paths are available which involve the ions $Fe(SCN)^{++}$ and $Fe(SCN)_2^+$, respectively. Laurence suggests a hydrogen atom transfer in the rate steps (77). Sheppard & Wahl (78) find a simple second-order law for the exchange between permanganate and manganate ions in alkaline solution; the work includes a study of salt effects. Fast isotopic exchanges between Ir(III) and Ir(V) complex halides are reported by Grinberg (79).

Marcus (80) has extended and applied his previously developed theory of electron transfer reactions not involving atom transfer, to both inorganic and organic systems; satisfactory agreement between theory and experiment is found for the system: $MnO_4^- —MnO_4^{--}$, $Fe(CN)_6^{4-}—Fe(CN)_6^{3-}$ $\cdot Mo(CN)_8^{4-}—Mo(CN)_8^{3-}$ and others. The theories of oxidation-reduction reactions are also reviewed by Marcus (81).

Other oxidation-reduction reactions.—The reaction of Fe^{++} ions with hydrogen peroxide has been re-examined by Hardwick with respect to analytical methods and reaction media (82). Dainton & Hardwick (83) have determined the reactivity of hydroxyl radicals with hydrogen and carbon monoxide by measuring the excess of ferric ions produced when the Fenton reaction is made to occur in presence of H_2 (CO). These results have been used by Hardwick (84) to derive an expression for the rate of oxidation of Fe^{++} by H_2O_2 in presence of H_2 (CO). Coppinger (85) has given direct evidence for the formation of hydroperoxy radicals in the metal ion-catalyzed decomposition of H_2O_2. Baxendale & Wells (86) found that in the reduction of Co(III) by water in perchlorate media, the rate shows a 3/2 dependence on Co(III) and is inversely proportional to $[H^+]^2$. In order to account for these findings it is necessary to assume that Co(III) is predominantly in a dimeric form; some kinetic data on the reduction of Co(III) in sulfate media are reported by Sharp (87).

Halpern & Webster (88) have extended their investigations on the homogeneous reactions of hydrogen in solution to the reduction of permanganate, both uncatalyzed and catalyzed by silver salts, and to the catalyzed reduction of dichromate. For the latter, Rate $= k[Ag^+]^2[H_2] + k_1[Ag^+]^2[H_2]/[Ag^+]$. The above expression is interpreted by assuming the formation of the reactive intermediates AgH^+ and AgH in two independent reaction paths. Evidence for AgH is obtained also from the isotopic exchange between the hydrogen in the gas phase and the deuterated water solvent. The effect of complexing agents upon the rate of silver ion reduction by hydrogen is also being studied (89).

In strong sulfuric acid the decomposition of Caro's acid, catalyzed by nitric acid, is second-order in the catalyst and presents the unusual feature that the order with respect to the peroxide ranges from -1 to 1, depending on the sulfuric acid concentration. The kinetic scheme assumes the formation

of a species HSO_5NO_2 which reacts with a nitronium ion in the slow step [Kuhn (90)]. Metal ion-catalysis in the decomposition of peroxydisulfuric acid is studied by Szabo' et al. (91). Longstaff (92) proposes the decomposition of the species $N_2O_3BrH^+$ in the slow step of the oxidation of bromide ions in aqueous nitric acid.

In the disproportionation of hypochlorous acid, the formation of chlorate is given by $Rate = [HClO]^2[ClO^-]$. D'Ans & Freund (93) propose the decomposition of the adduct $H_2Cl_3O_3^-$ as rate determining; but Abel (94) suggests that the reaction may go by way of chlorine monoxide formed in a prior equilibrium. The oxidation of sulfite by chlorate is first-order both in ClO_3^- and H_2SO_3; OH and HSO_3 radicals are tentatively suggested as reactive intermediates [Gleason et al. (95)]. Other studies concerning the oxidation of sulfite are reported by Higginson & Marshall (96) and Pirt et al. (97). The acid-promoted disproportionation of Nb(IV) is studied by Cozzi et al. (98).

Oxidation of organic substances by inorganic oxidants.—A variety of mechanisms seem to be available for the oxidation of organic substances by permanganate. In the oxidation of benzhydrol there is no transfer of oxygen from permanganate, and α-deuteration decreases the rate by a factor of 6.6; a hydride transfer from benzhydroxy ion to permanganate seems likely to take place in the slow step [Stewart (99)]. On the other hand, almost complete transfer of oxygen takes place in the hydroxylation of olefins, confirming the fact that a cyclic intermediate is involved [Wiberg & Saegebarth (100)]. These authors have discussed also the factors affecting the relative yields of diol and ketol formed in the oxidation and propose that a common intermediate be formed for which hydroxy and permanganate ions compete. The oxidation of lactic acid by permanganate is studied by Senent et al. (101). Bulgrin (102) finds that in the periodate oxidation of cyclopentane 1,2-diols, the trans isomer reacts more slowly.

The oxidation of olefins by Co(III) in aqueous sulfuric acid follows a second-order rate law; medium and structural effects are consistent with a rate-determining electron transfer from the olefin to Co(III) to give the ion-radical $R\text{—}CH\text{—}CH_2^+$. In glacial acetic acid Co(III) is unable to oxidize olefins; oxidation takes place upon addition of sulfuric acid but the rate becomes independent of olefin concentration [Bawn & Sharp (103)]. The oxidation of monosaccharides by Cu(II) is studied by Singh & Ghosh (104), and the oxidation of ethanol by Ce(IV) by Ardon who has found that the rate step is the decomposition of an intermediate formed by one ceric ion and one ethanol molecule (105).

Studies involving coordination compounds.—Posey & Taube (106) have attacked the problem of the mechanism of aquation of hexacoordinated complexes in water solvent. The metal ion-induced aquation of $Co(NH_3)_5X^{++}$ ($X = Cl$, Br, I) is being studied by two methods, using the competition (a) between water and added anions and (b) between isotopically different forms of water. The nature of the metal ion inducing the reaction appears to be an important factor in determining the reaction mechanism. Thus, while for

Hg^{++}-induced reactions the mechanism adheres strictly to the definition of the S_N1 mechanism, for the reactions induced by Ag^+ and Tl^{3+} a concerted process seems more likely in which the Co-X bond is broken while the Co—O bond is formed.

Rates and activation parameters for aquation of $Cr(en)_2Cl_2^+$ and $Co(en)_2Cl_2^+$ are very similar, suggesting that the same mechanism is operative in both reactions [Selbin & Bailar (107)]. This analogy probably reflects the similarity of orbital hybridization involved in Cr(III) and Co(III) complexes.

A number of recent papers deal with the dissociation of phenanthroline complexes. In acid solution the rate of dissociation of Fe(II) and Fe(III) complexes is affected by the presence of acids and salts. The large effect on both dissociation and racemization of the Fe(III) complex is attributable to specific ionic interactions. Spectral evidence confirms ion-pair formation [Basolo *et al.* (108)]. In alkaline solution, the rate of dissociation for the Fe(II) complex is greatly enhanced [Margerum (109)]; to account for the rate equation which contains zero, first, second, and even third power terms in OH^-, several intermediates are postulated, which contain mono-coordinated phenanthroline groups. In sharp contrast are the results which are found for the Ni(II) complex [Wilkins & Williams (110)]. In water and in a variety of other solvents the exchange between the complex and phenanthroline is independent of both phenanthroline and OH^- concentrations up to pH 13; only above this value a rate enhancement is observed both for exchange and racemization.

The substitution reactions of a number of Pt(II) complexes by a variety of nucleophilic reagents in aqueous solution have been investigated by Basolo *et al.* (111), who have given special attention to the so-called *trans*-effect. Two classes of reactions have been recognized which are (*a*) zero-order and (*b*) first-order in the substituting reagent; for reactions of class (*a*), the rate of substitution with a given complex is nearly independent of the nature of the reactant. Moreover, reactants which give rise to class (*a*) reactions have a low *trans*-effect. The mechanism proposed takes into consideration the fact that in square planar complexes, two other groups (solvent molecules and anions) are coordinated above and below the plane; the rate determining step would be a concerted process in which these two groups move in to assist the release of the leaving ligand. Other papers which deal with Pt(II) complexes are those of Chatt & Ahrland (112) and of Irving & Magnusson (113).

Isotopic exchanges between complex halides of Cr(II), Pd(II), Pt(II), and Pt(IV) and halide ions have been reported by several authors (114). Adell (115) has found that the isomerization of Co(III) dinitro complexes to the corresponding nitrito form follows first-order kinetics and probably involves the nitrito-nitro form as intermediate.

Tracer studies.—The fast chlorine exchange found by Norris & Johnson between thionyl chloride and bromide (116) suggests some kind of self-ionization equilibria such as $2 SOCl_2 \rightleftharpoons SOCl^+ + SOCl_3^-$, etc., involving $SOBr_2$. This

finding raises the question of whether or not the above mechanism is respons-
ible for the rapid halogen exchange occurring between halide ions and non-
metal halides and oxyhalides. The results reported by Lewis & Sowerby (117)
show that this is probably not the case. In fact, in carbon tetrachloride, the
exchange between tetraalkylammonium chlorides and $POCl_3$ occurs by way
of a bimolecular mechanism which probably involves the reversible forma-
tion of $[POCl_4]^-$ ions; therefore, although self-ionization may in general be
operative, the associative mechanism is likely to provide an easier path.
Lewis & Sowerby (118) have also studied the exchange of chlorine between
nitrosyl chloride and a number of covalent chlorides and oxychlorides. The
fast exchange occurring with $FeCl_3$, $SbCl_3$, and $AsCl_3$ appears to arise from
the formation of the relatively stable nitrosonium salts. In chloroform, rapid
exchange has been found by Frazer between pyridinium chloride and BCl_3,
PCl_3, $SOCl_2$, SO_2Cl_2, and CH_3COCl (119). In carbon tetrachloride, PCl_3 and
PCl_5 exchange chlorine (or phosphorous), and the rate is independent of
PCl_3 concentration; apparently the dissociation, $PCl_5 \rightarrow PCl_3 + Cl_2$, is rate de-
termining [Johnson & Becker (120)]. Rate and activation parameters for the
exchange between Sn(II) and Sn(IV) chlorides in methanol are presented
by Meyer & Melnick (121). Iodine cyanide seems to exchange with iodide and
cyanide ions in water and in various organic solvent, and, with iodine in
heptane, within the time required for separation [Jenkins & Harris (122)];
that the latter exchange is very fast, seems puzzling. Since extraction with
water was used for separation, the exchange might have arisen from the fast
hydrolytic equilibria of either species; alternatively, if no provision were
made to exclude light, photochemical exchange could have occurred. Swain
and his co-workers (123) have investigated the exchange of hydrogen be-
tween hydroxyl and ammonium compounds both in an inert solvent and in
pure alcohols, using a variety of alkylammonium salts. The reaction is first-
order both in the hydroxyl and ammonium compounds, and very nearly de-
pends upon the inverse first power of the acid concentration. The mechanism
proposed assumes the formation of a hydrogen bonded intermediate of the
type, $[RO^- \ldots H^+NR_3]$ or $[ROH \ldots NR_3]$. A simple second-order rate law
is found by Nefedov *et al.* (124) for the exchange of mercury between
CH_3HgBr and $HgBr_2$ in ethanol. The oxygen exchange between water and
sulfuric acid is first-order with respect to both H^+ and HSO_4^-; Hoering &
Kennedy propose that the rate step is the dissociation of sulfuric acid to give
water and sulfur trioxide (125). Mechanistic tracer studies have been re-
viewed by Stranks & Wilkins (126).

Miscellaneous inorganic reactions.—Interesting salt effects are reported
by Indelli (127) for the alkaline hydration of tri- and tetrametaphosphate.
While the bimolecular constants calculated from initial rates increase with
concentration, as should be expected on the basis of the ionic strength in-
crease, in any given run the bimolecular constants decrease during the course
of the reaction, despite the increase in ionic strength. This and other effects
are interpreted in terms of ionic association and secondary salt effects. The

neutral and acid hydrolysis of condensed phosphates have been extensively treated by Thilo and his colleagues (128). Seel *et al.* (129) find that the hydrolysis of nitrilosulfonate ions involves the formation of the first conjugate acid, $HN(SO_3)_3^{--}$; the work includes a study of salt effects. Smith (130) has found that the rate of association of ferric ions with fluoride ions in perchloric acid is of the order of 10^2 l. mole^{-1}sec.$^{-1}$

ORGANIC REACTIONS

Acid-base catalysis.—The Zucker-Hammett criterion has been extensively used in the past year to determine whether, in an acid-catalyzed reaction in an aqueous medium, the transition state does or does not contain a water molecule. At the same time, however, the limitations of the criterion are becoming more clearly understood. Fundamental in this respect is the work of Deno & Perizzolo (131). From the definitions of acidity functions and from the Brønsted form of the rate law, they derive expressions (which contain the activity coefficients of cations and neutral molecules) relating the rate constant with acidity functions. On the basis of these expressions, it would be possible to make reasonable predictions as to the form of the rate law if the variation of the activity coefficients with acid strength were known for a large number of cations and neutral molecules. For this purpose, Deno and Perizzolo determine the activity coefficients for a number of representative neutral molecules and salts in water-sulfuric acid mixtures, and indicate how these results can be used. The fact that reactions whose transition state contains a water molecule, usually show a linear dependence on acid concentration, rather than on h_o, is considered merely coincidental by these authors; it simply bears out the circumstance that in most of these examples there is an unshielded charge at the transition state so that the ratio $f_{H_3O}^+/f_X^{\ddagger}$ is constant. Transition states could be envisaged in which, although containing a water molecule, the charge is well shielded from the solvent; the above ratio would no longer remain constant, and the rate would tend to vary as h_o. Evidence concerning the limitation of the Zucker-Hammett criterion has also been presented by Grunwald *et al.* (132), and Satchell (133) has discussed the limits of its applicability to reactions in mixed solvents.

Many papers have been published concerning the mechanism of ester hydrolysis; kinetic as well as tracer methods have been used to discover whether in particular examples, acyl-oxygen or alkyl-oxygen fission takes place. Bunton *et al.* (134) have found that diphenylformate and acetate undergo Ac—O fission both in basic and acid hydrolysis, while in neutral hydrolysis Al—O fission occurs to some extent. On the other hand, *p*-methoxydiphenyl formate undergoes Al—O fission in neutral and acid hydrolysis, the rate being proportional to h_o (135). Salomaa (136) has made a thorough study of the acid-catalyzed hydrolysis of alkoxymethyl esters, $RCOOCH_2OR'$; Al—O fission prevails. However, when $R' = H$ both of the mechanisms become of comparable importance. Salomaa (137) and Bell & Lukianenko (138) find no evidence of Al—O fission in the acid-catalyzed hydrolysis of

methylene and ethylidene diacetates. Ac—O fission also occurs in the acid-catalyzed hydrolysis of chloromethyl acetate [Euranto (139)]; the work includes a detailed study of solvent effects.

The imidazole-catalyzed hydrolysis of phenylacetates has been studied by Bender & Turnquest (140) and Bruice & Schmir (141), who find the reaction to be first-order in both ester and free imidazole. The results are consistent with a mechanism in which imidazole attacks the carbonyl-carbon giving N-acetylimidazole which, in turn, is hydrolyzed by water, regenerating the catalyst; substituent effects corroborate the above mechanism. Substituent effects on the rate of alkaline hydrolysis of esters of benzylidene-pyruvic acid have been studied by Stecher *et al.* (142). The amine-catalyzed hydrolysis of phenyl acetates has features which are typical of general base-catalysis [Bender & Turnquest (143)]. Since, in these reactions, the rate step does not involve the transfer of a proton from the substrate to a general base, it is suggested that the latter may not be a necessary requirement for general base-catalysis to be observed; a reaction, in which the rate-determining step is the introduction of a base into the substrate to give an unstable intermediate, may exhibit general base-catalysis as well. Bartlett and his co-workers (144) find that the reaction of the Leuchs anhydrides with water is subject to general base-catalysis and is not catalyzed by acid. They discuss the possibility of controlled peptide synthesis from Leuchs anhydrides in aqueous solutions. Interesting solvent effects in the neutral hydrolysis of acyl esters of salicylic acid are reported by Garrett (145), who also reports evidence of general base-catalysis in the hydrolysis of an alkyl aminoacetylsalicylate (146). Metal ion-catalysis in ester solvolysis has been reported by Hoppe' & Prue (147) and by Bender & Turnquest (148); specific ionic interactions (chelate formation) are assumed.

The solvolysis of amides and related compounds is studied by Marvell *et al.* (149), Edward & Meacock (150), and Tirouflet *et al.* (151); Taft & Biechler (152) discuss in great detail the mechanism of alkaline hydrolysis of anilides. Newman *et al.* (153) find that hindered aromatic amides may be dehydrated by alkali to the corresponding nitriles, probably by way of a base-catalyzed elimination of the enol form of the amide. Acid catalysis and salt effect in the hydrolysis of murexide is studied by Ramaiah *et al.* (154). The hydrolysis of thioacetamide is studied by Butler & Swift (155) in the presence of As(V) and As(III), and by Rosenthal & Taylor (156); the latter propose a mechanism in which both thionamido and thiolimido tautomeric forms of thioacetamide are involved.

Salomaa (157) studies the acid-catalyzed solvolysis of ethylate in water-ethanol mixtures; the results can be accounted for by assuming the formation of an alkoxymethyl cation for which water competes against ethanol. Dunn (158) reports that the hydrolysis of methoxymethylurea is subject to general acid-base catalysis and proceeds according to a two-step reaction in which hydroxymethylurea is formed first. Consistent results have been obtained for the alkaline hydrolysis by Ugelstad & de Jonge (159), who propose a

mechanism similar to that assumed for hemiacetals hydrolysis; other pertinent studies are those of Landqvist (160). Long *et al.* (161) have considered the entropy of activation as a criterion for distinguishing the uni- and bimolecular mechanism in the acid-catalyzed hydrolysis of ethylene oxides. The results are consistent with the unimolecular mechanism being operative for the series of the methyl substituted ethylene oxides and for trimethylene oxide. The electrolyte catalysis and kinetics of benzyl phenyl ether cleavage by HBr is studied by Drummond & Eastham (162) in nitrobenzene, chloroform, and carbon tetrachloride; and Burwell & Fuller (163) calculate the relative rates of C—O fission in the internal competitive reaction: $ROR' + HBr \rightarrow (R'Br, RBr) + (ROH, R'OH)$. A thorough study of the alkaline mutarotation of D-glucose is made by Los & Simpson (164) who give the catalytic constants and activation parameters for α- and β-glucosate ions; experimental technique and handling of data are reported in great detail.

Carbonium ions.—The acid-catalyzed oxygen exchange between water and alcohols has been studied by Grunwald *et al.* (132) and by Bunton & Llewellyn (165); the latter find that the rate of racemization of *sec*-butyl alcohol is twice as fast as the rate of exchange, but, with increasing acid concentration, the ratio k_{rac}/k_{exch} becomes less than two. This can be explained if allowance is made for the concurrent reversible elimination reaction. On the other hand, Grunwald *et al.* find $k_{rac}/k_{exch} = 1.2$ for 1-phenylethyl alcohol and discuss this and other results in terms of carbonium ion stability and shielding by the leaving group. I. Wilson [unpublished results quoted by Bunton (165)] finds that 4,4'-dimethoxybenzhydryl alcohol racemizes at the same rate as it exchanges oxygen. Although Grunwald's description seems indeed very sound, it appears that Streitwieser's (166) theory of solvolytic reactions also provides a very neat interpretation; according to this theory it has to be expected that, as the carbonium ion becomes intrinsically more stable, i.e., the more it may internally disperse the charge, k_{rac}/k_{exch} tends to one, in line with the results above.

Deno *et al.* (167) have studied the acid-catalyzed reaction of *t*-butyl alcohol with acrylonitrile and propionitrile in water and find, $Rate = k[RCN][ROH]h_o$. The authors' interpretation is that the reaction is a direct displacement in which the incoming nucleophile (the nitrile) makes only a weak bond with the central carbon.

The product-determining step in the reaction between aliphatic amines and nitrous acid is kinetically inaccessible; any deduction concerning the mechanism must then be inferred from indirect evidence. Since the commonly accepted mechanism (according to which the product step consists of the bimolecular displacement by a solvent molecule on the alkyldiazonium ion, competing with the unimolecular splitting to give a carbonium ion), fails in many instances to account for the observed product distribution, it has been proposed that the resulting carbonium ion is left in an exceptionally high energy state. In this respect it differs from a carbonium ion produced in solvolysis. Cram (168) shares this view and argues that, since in the diazo-

nium ion dissociation the elimination of the nitrogen molecule essentially provides the driving force, there should not be significant neighboring group or solvent participation at the transition state; thus, the fate of this "little solvated," "hot" carbonium ion is determined by which groups happen to be closest to the reaction center, not by their nucleophilicity. Therefore, the stereochemical outcome may be rationalized in terms of the relative conformational populations of the starting diazotized amine. Streitwieser & Schaeffer (169) present a contrasting viewpoint, the essential feature of which is that the diazonium ion is a common intermediate for several competing reactions, including dissociation, to give an "ordinary" carbonium ion. His line of thought is expressed as follows: in all reactions of the diazonium ion where the driving force is provided by the elimination of the nitrogen molecule, the activation energies are very small (probably of the same order as for rotation about a C—C bond) and the transition states closely resemble the reactants much more than in solvolysis reactions; consequently, all reactions having very small activation energies, although percentagewise considerably different, have a chance to compete successfully with one another and with carbonium ion formation. On this basis, Streitwieser & Schaeffer (170) have neatly interpreted a good deal of the existing data.

Carbanions and base-catalyzed elimination reactions.—Hine *et al.* (171) have measured the hydroxide ion-catalyzed hydrogen exchange between deuterohaloforms and water and find that α-halogen atoms facilitate carbanion formation in the order, $I \sim Br > Cl > F$; the sequence above appears to be result of a blend of inductive, resonance, and polarizability effects. Taft (172) has correlated the rates of carbanion formation of several substituted methanes by means of a free energy relationship in which inductive and resonance interactions are separated into two independent contributions [see also Taft (173)]. The values of the constants for susceptibility to inductive and resonance interactions suggest that the latter are relatively much more important when the substituent is directly attached to the reaction center than when the same substituent acts through a mesomeric system.

A number of important contributions have cast considerable light on the nature of the transition state in base-catalyzed elimination reactions; open chain as well as cyclic systems have been investigated. Goering *et al.* (174) find that *cis*-chlorocycloalkyl aryl sulfones eliminate more rapidly than the corresponding *trans*-isomers and the rate is enhanced by electron-attracting substituents in the aryl moiety; it is apparent that *trans*-compounds undergo *cis*-elimination and this is suggested to be a two-step process involving carbanion formation. Analogous views are shared by Cristol & Arganbright (175) who show that *cis*-elimination may be preferred in cases where the groups are held rigidly in positions in order that the coplanarity required for *trans*-elimination is not easily attained. For instance, *trans*-2,3-dichloronorbornane reacts about 85 times faster than the *cis*-isomer; carbanion formation is suggested by the large increase in reactivity which occurs upon introduction of a *trans*-sulfone grouping.

The possibility of carbanion formation when powerful electron-attracting substituents are in the β-position was tested by Skell & McNamara (176) and by Bordwell & Landis (177). Their approach has been through the study of the elimination reaction in an open-chain system starting from pure diastereomers. If the reaction were a two-step process with a carbanion intermediate, elimination would yield the same product irrespective of the starting material. The results show that elimination in an open-chain system is stereospecific and, consequently, a carbanion intermediate of any but extremely short life is excluded. The comparison of the rates for the open chain with a corresponding cyclic system (five ring) shows that in the latter *trans*- and *cis*-elimination occur at about the same rate, and only slightly faster than in the open-chain system. These considerations lead Bordwell & Landis to conclude that *cis*-elimination occurs in a concerted one-step process. Saunders & Asperger have attacked the problem by studying the sulfur isotope effect in the elimination of 2-phenylethyl dimethylsulfonium iodide; the effect found is very small, indicating that in the activation process the rupture of the C—S bond has only proceeded slightly; thus, the transition state has considerable carbanion character (178). Further information has been provided by the study of substituent effects in the reaction of *p*- and *m*-substituted 2-phenylethyl halides, tosylates, and sulfonium salts [DePuy and co-workers (179), and Saunders & Williams (180)]; the rate data fit the Hammett equation with positive ρ. The results are discussed by Saunders & Williams on the basis of the possible structures for the transition state:

$$
\begin{array}{ccc}
X & X & X \\
| & | & | \\
C_2\text{----}C_1 & C_2\text{----}C_1 & C_2\text{----}C_1 \\
| & \vdots & \vdots \\
H & H & H \\
\vdots & \vdots & | \\
B & B & B \\
\text{I} & \text{II} & \text{III}
\end{array}
$$
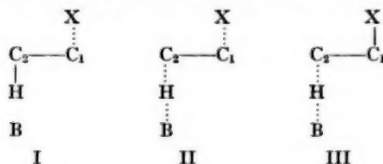
The structures above are the conventional representation for *E 1*, *E 2*, and *E 1 cb* elimination, respectively. In any actual case the transition state will always be something intermediate between these structures, the prevalence of any one of them being determined, in a given medium and for a given base, by the nature of the substituents at C_1 and C_2. Thus, electron-attracting substituents at C_2 can stabilize the developing negative charge and consequently shift the transition state toward III; if III is prevalent, there is no significant double bond character at the C—C bond and, therefore, in a cyclic system *cis*-elimination will be less disfavored with respect to *trans*-elimination. Other factors (steric, for instance) may become predominant in determining the rate and the course of the reaction. This unifying picture, very similar to that previously given by Cram (181) in a discussion of medium and leaving group effects, seems best equipped to accommodate all experimental results; it does not exclude the assumption that, as also suggested by Bordwell, in proper structural and environmental conditions the carbanion structure be eventually attained.

Aromatic systems.—A number of theories have been introduced in recent years which correlate the reactivity of conjugated systems to such theoretical quantities as self-polarizability, π-electron density, free valence, localization energy, etc. Although the starting assumptions from which these quantities are derived differ from one another, there is considerable agreement as far as the predictions of these theories are concerned. That this is not casual, has been demonstrated by some Japanese workers, by showing how these quantities are mathematically correlated [Fukui *et al.* (182); Baba (183)]. A new quantity of more general character, the partial polarization energy, has been introduced by the latter author.

Several workers have continued to apply the quantities above to the correlation of experimental data. Berliner & Shieh (184) measured the rates of solvolysis of polynuclear α-arylethyl chlorides and found that the relative reactivities agree with theoretical predictions, except for compounds having a "α-naphthalene-like" structure. The same observation has been made by Okamoto & Brown (185) and by Dewar & Sampson (186) and is consistently attributed to steric interactions at the transition state, involving the *peri* grouping. Dewar & Sampson (187) reported the rate of solvolysis of polynuclear arylmethyl chlorides in formic acid and in aqueous ethanol; they also developed a molecular orbital treatment for nucleophilic displacement reactions in which, in a series of compounds in a given solvent, there is transition from the limiting to the fully assisted mechanism.

Brown and his co-workers (188, 189) have measured the rates of solvolysis of a series of substituted phenyldimethylcarbinyl chlorides in aqueous acetone and, using these data, have constructed a new set of substituent constants, σ^+, applicable to aromatic electrophilic substitutions and side-chain reactions involving large resonance interactions between the substituent and the reaction center. This new set is used to analyze available data concerning electrophilic reactions of various kinds and is shown to provide a better fit than is commonly obtained by using the σ constants (190). The results concerning *meta*- and *para*-alkyl substituted compounds are quite interesting (188). In the *meta* series the rate sequence follows the hyperconjugative order (Me $>$ Et $> i-$Pr $> t-$Bu); the same order (Me $> t-$Bu) is found in the solvolysis of benzhydryl chlorides by Shiner & Verbanic (191) who, in addition, observe that the hyperconjugative sequence may be turned into the inductive one by merely changing the solvent from aqueous acetone to aqueous alcohol. The *para* series follows, as expected, the hyperconjugative sequence. However, the fact that the ratio, $k_{p-t-\text{Bu}}/k_{m-t-\text{Bu}}$, is of the same order as $k_{p-\text{Me}}/k_{m-\text{Me}}$, leads Brown to suggest that, since the inductive effects of the alkyl groups in the *m*- and *p*- positions should not differ greatly, the extra-stabilization of the transition state introduced by the *p-t*-butyl group is due to carbon to carbon hyperconjugation; the magnitude of the C—C hyperconjugative effect relative to C—H is estimated to be about 0.8.

The effects of *p*- and *m*-alkyl substituents (α- and β-branched) has been studied by Shiner & Verbanic with special regard to solvent effects (191). A log/log plot of the relative rates in one solvent versus the relative rates in

another is not linear, but the derivatives with the more highly branched substituents react more slowly in the more polar solvents. The effect can be ascribed either to solvation enhancement of hyperconjugation or to steric inhibition of solvation.

Several papers have appeared which deal with the relative reactivity of different positions of aromatics. Lerer *et al.* (192) measure the isomer distribution in the chlorination of *t*-butylbenzene, while De la Mare & Harvey (193) study bromination by hypobromous acid. Similar studies on diphenyl have been made by De la Mare & Hassan (194) and Simamura & Mizuno (195); as expected, the *o*- and *p*- positions are activated and the *m*-positions deactivated with respect to one position of benzene. Brown & Young (196) determine the rates of the aluminum chloride-catalyzed benzoylation of benzene and toluene; the relative rate benzene/toluene agrees very closely with the value calculated from the isomer distribution using the previously developed relationships between the partial rate factors and the "selectivity factor" [Brown & Smoot (197)]. These relations have also been applied by Brown & Stock (198) to calculate the relative rates of bromination and chlorination for the whole series of methylbenzenes. Considering the wide spread in reactivity, the agreement between calculated and experimental values is remarkably close.

The relative rates p-/m- for bromination are difficult to measure since the amount of m- product is often small to the point of vanishing. The problem has been solved by Illuminati & Marino (199) by measuring the rate of bromination of halomethylbenzenes having either the m- or p- position available. The partial rate factors p-/m- so obtained for halobenzenes are: PhF, 2230; PhCl, 128; PhBr, 58; PhI, 18. Illuminati (200) finds agreement between the observed rate of bromination of nitromesitylene and the rate predicted on the basis of the Hammett equation (using Brown's σ^+); this would not be expected to apply, should any effect of reduced conjugation due to noncoplanarity of nitromesitylene be operative.

Dewar has pursued his studies of electrophilic aromatic substitution. The kinetics of chlorination of several polycyclic hydrocarbons are studied in acetic acid and in carbon tetrachloride, and rates lower by a factor of 10^3 are reported in the latter solvent (201). Nitration of quinoline in sulfuric acid yields essentially the expected 5- and 8- isomers but in acetic acid the 3-isomer is predominant; Dewar suggests that in this medium the species undergoing reaction is not quinoline itself, but an added product to the 1,2 bond (202). The observed isomer distribution in the nitration of several six-membered, nitrogen-containing heterocycles fits quite well with the predicted relative reactivity of the various positions (203).

Shatenshteĭn *et al.* have measured the rate of exchange between DBr and a variety of polycyclic hydrocarbons, and substituted benzenes and naphthalenes (204). Machor *et al.* (205) find that the rate of hydrogen exchange between deuterated alkylbenzenes and the solvent (trifluoroacetic-sulfuric acids mixture) is proportional to h_o; one alkyl group o- or p- to the deuterium atom increases the rate by a factor of 10^3.

The halogenation of aromatics by molecular halogens displays complex rate laws containing the first, the second, or even the third power of the halogen concentration; the importance of the various terms varies widely according to the solvent composition, and in the more polar solvents the first power term may become predominant. This behaviour may be interpreted by assuming a fast equilibrium between the aromatic and one-halogen molecule (formation of a π-complex) followed by the slow reaction of the complex with one electrophilic molecule (E) whose role is to remove the halide ion:

$$ArH+X_2 \rightarrow ArH. \; X_2 \underset{+E}{\overset{slow}{\longrightarrow}} ArHX^+ + EX^-.$$
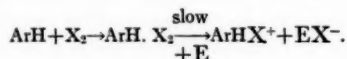
The absence of a hydrogen isotope effect requires that the proton be removed in a subsequent fast step. The role of E may be taken by a second halogen molecule (or by a dimer of it), by a catalyst, or, if the solvent is able to play such a role, by a solvent molecule. Hence, a variety of kinetic laws may result according to the nature of the halogenating agent and the solvent. Results in this field which are in general agreement with the above picture have been obtained by Andrews & Keefer (206), Berliner & Beckett (207), and Gnanapragasam (208).

While the formation of a discrete intermediate in electrophilic aromatic substitution is generally accepted [see, for instance, Cannell (209); Gore (210)], the nature of the transition state leading to it is rather indefinite. Interesting observations concerning this point have been made by Heck & Winstein (211) and Corey & Sauers (212) in the study of the aryl group participation in the solvolysis of ω-aryl-1-alkyl benzenesulfonates.[3] For Ar_1- assisted solvolysis a maximum of participation obtains for $n = 5$, while for Ar_2- the maximum occurs for $n = 6$. Simple steric considerations show that the observed behaviour is indeed expected if the approach of C_α to Ar occurs in a direction perpendicular to the benzene ring. Therefore, of the two possible extreme structures, A and B, for the transition state,
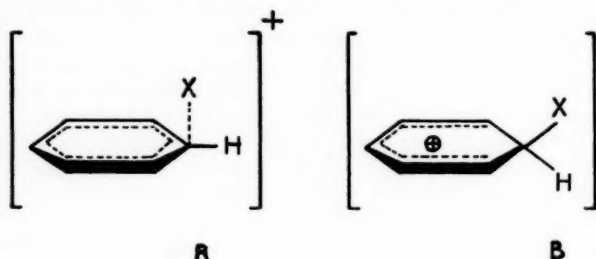
A is more near to the truth; this conclusion, while holding for these particular solvolyses, has probably more general validity.

[3] In Winstein's notation for anchimerically assisted ionization, Ar_a-n, a indicates the position of the aryl group, Ar, participating to the formation of the n-ring.

A concept analogous to the kinetic isotope effect, the "element effect," has been applied by Bunnett *et al.* (213) to aromatic nucleophilic substitution. They have found that several substituted 2,4-dinitrobenzenes react toward piperidine at about the same rate in spite of the fact that the bonds being broken in these substitutions involve five different elements (Cl, Br, I, O, S). The constancy of the rates signifies that bond breaking has not proceeded very far in the activation process, suggesting that a relatively stable intermediate is formed in the slow step. On the other hand, large rate variations may arise when the group being displaced is a very strong electron-attractor; in these cases either no intermediate is formed or, more likely, the dissociation of the intermediate is rate determining.

Capon & Chapman (214) study the effect of nuclear alkyl substitution in the dechlorination of chlorodinitrobenzenes by a number of nucleophiles and discuss a variety of steric and electronic effects. Other studies concern the reactions of bromonitronaphthalenes (215) and 2- halofurans (216) with piperidine, the exchange between iodide ion and iodobenzene (217), and the effect of p-CN and p-CHO in the substitution of 4-iodo-3-nitrobenzene with thiocyanate. This work includes a comparison of the nucleophilicities of methoxide, azide, phenoxide, and thiocyanate ions [Miller *et al.* (218)]. Bottini & Roberts (219) find that two mechanisms, elimination-addition and direct displacement, are available for the alkaline hydrolysis of halotoluenes.

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QUANTUM THEORY OF ELECTRONIC STRUCTURE OF MOLECULES[1,2]

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This review will cover the recent development in the theory of electronic structure of molecules. It starts with the description of recent studies on the helium atom, which show how reliable quantum mechanics is as the foundation for the whole story. Then follows the nonempirical theory of simple molecules. Various semiempirical theories of molecules will be discussed next, and results of calculation of various molecular constants will be reviewed. In this review only papers published in 1957 and those closely related to them will be surveyed.

Nonempirical Theory

Theory of the helium atom.—Quantum theory of (simple) molecules is essentially a special field of the theory of many electron systems; and for the reason that in the case of two electron systems a precision comparable to that of spectroscopic measurements can be attained from purely theoretical calculation, the study of the simplest two-electron system, i.e., of the helium atom, is highly important to molecular scientists though the helium atom is an atom, not a molecule. Particularly the recent revival of the interest in the helium problem is due to the fact that on the one hand the ionization potential of the helium atom was measured with high accuracy by Herzberg & Zbinden (1), and on the other hand the quantum-electrodynamical correction to the term value, known as Lamb shift (2), and relativistic corrections were estimated theoretically. Under these circumstances the revision and extension of Hylleraas' calculation (3) have been regarded necessary, and several authors undertook the work of calculating the lowest eigenvalue of the nonrelativistic Hamiltonian of two-electron atoms as accurately as possible.

As is well-known, Hylleraas employed the series

$$\Psi = e^{-(1/2)s} \sum_{lmn} c_{lmn} s^l t^m u^n \qquad \text{I}$$

where $s = r_1 + r_2$, $t = r_1 - r_2$, $u = r_{12}$ and l, m, n are positive integers or zero.

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[1] The survey of literature pertaining to this review was concluded December, 1957.

[2] The following abbreviations will be used: CI, configuration interaction; HL, Heitler-London; LCAO, linear combination of atomic orbitals; MO, molecular orbital; SCF, self-consistent field; VB, valence bond; HF, Hartree-Fock; DAIM, deformed atoms in molecule; AIM, method of atoms in molecule; AO, atomic orbital; ASMO, antisymmetrized molecular orbital; ICC, intra-atomic correlation correction.

Herzberg & Chandrasekhar (4) used expressions of this form as trial functions in the variational calculation for He atom, and obtained an improved result by increasing the number of terms in the expansion. On the other hand, Schwarz (5), Hylleraas & Midtdal (6) and Kinoshita (7) attempted to make the convergence more rapid by introducing additional freedoms into the series: Schwarz allowed l, m, or n to take half-integral values besides integral values; the convergence was thereby improved, but Kinoshita remarked that with the use of such functions the relativistic corrections would diverge. Both Herzberg & Midtdal and Kinoshita calculated not only the ordinary variational upper limit of the ground state energy, but also the corresponding lower limit. The lower limits estimated with the use of Hylleraas' functions were considerably lower than the upper limit, and this slow convergence is closely connected with the fact that the Hylleraas type series cannot be the formal solution of the Schrödinger equation even if the series is extended infinitely. To overcome this difficulty, Hylleraas & Midtdal added three negative power terms and one logarithmic term to a Hylleraas-type series of 20 terms, while Kinoshita assumed the trial wave function in the form:

$$\Psi = e^{-(1/2)s} \sum_{\lambda\mu\nu \geq 0} K\lambda\mu\nu (r_1 + r_2)^\lambda \left(\frac{r_{12}}{r_1 + r_2}\right)^\mu \left(\frac{r_1 - r_2}{r_{12}}\right)^\nu \qquad \text{II}$$

This series can be expressed in Hylleraas' form with $l = \lambda - \mu$, $m = \nu$, $n = \mu - \nu$, so that the original Hylleraas' assumption corresponds to the restriction $\lambda \geq \mu \geq \nu$. Kinoshita showed that by removing this restriction one can obtain the formal solution.

The nonrelativistic energy values calculated with the use of these series are given in Table I. Further Kinoshita showed that the difference of upper

TABLE I

CALCULATED VALUES OF NONRELATIVISTIC ENERGY OF THE HELIUM ATOM

	No. of terms	Energy (atomic units)
Hylleraas	6	-2.90324
Herzberg & Chandrasekhar	20	-2.903718
Schwarz	13	-2.903719
Hylleraas & Midtdal	24	-2.903729
Kinoshita	39	-2.903723

and lower bounds given by his 39 term function was as small as 120×10^{-6} au, and that the contamination of excited states in his (approximate) function was actually less than 0.1 per cent. Noting that $\sigma^2 = (\Psi|H^2|\Psi) - (\Psi|H|\Psi)^2$ decreases monotonously with the increase of the number of terms in the series, he estimated the most probable value of the energy by extrapolating the value of $E = (\Psi|H|\Psi)$ to $\sigma = 0$:

$$E = -2.9037237 \text{ au}.$$

Choice of orbitals to be used in configuration interaction calculations for the helium atom.—Hylleraas' & Kinoshita's method of series expansion is obviously the most powerful one proposed hitherto for the accurate treatment of two-electron atoms and ions, and James' & Coolidge's calculation (8) of the hydrogen molecule, which can be regarded as an adaptation of Hylleraas' theory to molecules, may also still have room for refinement similar to Kinoshita's. It is very difficult, however, to extend theories of this type to atoms and molecules with three and more electrons. For these atoms and molecules the method of configuration interaction (CI) is preferable if one wants to obtain an accuracy higher than that of the self-consistent field method.

In CI calculation the molecular wave function Ψ is assumed in the form of a linear combination of functions for several configurations:

$$\Psi = \sum_i c_i \Psi_i. \qquad\qquad \text{III}$$

Usually one includes a small number of terms in this sum, and each configurational function Ψ_i is related to some excited state of the molecule in a more or less approximate way. It is by no means necessary, however, that these Ψ_i's are good approximate wave functions for these excited states. Very often (III) takes such a form that the series may be interpreted as an expansion of the (true) wave function in terms of functions built from a given set of single electron functions (orbitals). In this respect one encounters the problem of choosing a suitable set of orbitals from which good wave functions can be constructed for the ground and lower excited states with a relatively small number of terms.

This problem has recently been studied, again for the case of the helium atom, by Taylor & Parr (9), Löwdin & Shull (10), Holøien (11), and Green, Chandler & Rush (12). In principle, the most rapid convergence will be obtained with the use of Löwdin natural orbitals, but unfortunately these natural orbitals can be constructed only after a fairly accurate wave function for the total system has been found, e.g., through CI calculation with some conventional set of orbitals. Taylor & Parr showed that if hydrogen-like functions are employed as orbitals in CI calculation of the ground state of He, the convergence is rather slow. According to Löwdin & Shull this slowness in convergence is due to the fact that the complete set of hydrogen-like functions contains a continuous spectrum. Another complete orthogonal set

$$(2\eta r)^l L_{n+l+1}^{2l+1}(2\eta r) e^{-\eta r} \times \text{(spherical harmonics)}, \qquad \eta = \text{const}, \qquad \text{IV}$$

involving associated Laguerre functions L_{n+l+1}^{2l+1} is completely discrete, and is convenient for use in CI calculation. The main difference between (IV) and the hydrogen-like functions is that in the former the "orbital exponent" η is common to all members of the set while in the latter it is inversely proportional to the principal quantum number n. Calculations by Löwdin & Shull and Holøien have made clear that the set (IV) is definitely superior to hydrogen-like functions as far as the rapidity of convergence is

concerned. Holøien included configurations of the type $(ns)(n's)$ up to $(6s)^2$, and estimated the so-called radial correlation energy by extrapolation. Further he showed that the large part of this radial correlation can be expressed as the in-and-out effect by using two different orbital exponents.

Green *et al.* also studied the ground state of helium by the method of configuration interaction. They took the radial part of orbitals in the form

$$R_{nl} = r^{l+1}e^{-\alpha(n,l)r} \sum_{\nu=0}^{n-l-1} a_{\nu}r^{\nu} \qquad \text{V}$$

and, assuming the superposition of 7 configurations $1s^2$, $1s2s$, $1s3s$, $2p^2$, $2p3p$, $3d^2$, $4f^2$, determined the best value of parameter $\alpha(n,l)$ for each of them. They found that, contrary to the case of hydrogen-like functions, $\alpha(n, l)$ tends to increase slightly with increasing n and l. The choice of a common orbital exponent ($\alpha(n, l)$ independent of n and l) increases the energy value only by 0.1 ev, which is still lower than that given by the Hartree field by about 1 ev.

Repulsion between two helium atoms.—The repulsive potential between two helium atoms is the simplest example of interaction potential between two closed systems, and for many years theoretical calculations of this potential as function of the internuclear distance R have been made by a number of authors. For large R the potential gives the so-called van der Waals interaction, which can be experimentally determined from the equation of state and the gaseous transport coefficients. For small values of R, the knowledge of the interaction potential is derived from experiments of scattering of high energy helium atoms in helium gas; in fact Amdur & Harkness (13), on analyzing their scattering experiments, found that the potential is much lower than those given by the HL method in which the wave function of the total system is constructed from the orbitals appropriate for free helium atoms. Some attempts were recently made to account for this discrepancy. First, Griffing & Wehner (14) calculated the electronic energy of a pair of helium atoms, assuming the configuration $\sigma_g{}^2\sigma_u{}^2$ with the LCAO

$$\sigma_g \propto e^{-Zr_a} + e^{-Zr_b}, \qquad \sigma_u \propto e^{-Zr_a} - e^{-Zr_b} \qquad \text{VI}$$

and succeeded in lowering the potential at $R=1$ au by 17 ev from the value given by the naive HL method. The optimum value of Z is found nearly equal to $27/16$, independent of R. Second, Sakamoto & Ishiguro (15) tried to improve the HL calculation by taking deformed atomic orbitals of Inui & Nordsieck's type (16)

$$e^{-Zr_a-Z'r_b}, \qquad e^{-Zr_b-Z'r_a}, \qquad z' < z \qquad \text{VII}$$

instead of e^{-Zr_a}, e^{-Zr_b}. By this method the energy at $R=1$ was further lowered by about 0.8 ev. Finally, Huzinaga (17) suggested that the orbital exponent of σ_u should be far smaller than that of σ_g from the consideration of correlation to the united atom Be, and carried out the ASMO calculation varying the orbital exponents of σ_g and σ_u independently. In this way further depression of about 12 ev was obtained. Thus, the MO method is far superior to

the HL method for the calculation of repulsion between closed shells, at least for sufficiently close encounters.

O_2 *and* Li_2 *molecules.*—O_2 is one of the most familiar molecules, for which we have relatively thorough information about various molecular properties. Hence it is worthwhile to carry out detailed calculation on this molecule and to examine the relative merits and demerits of various approximation methods. A study along this line was made by Kotani *et al.* (18). They used 10 Slater-type atomic orbitals, $1s_a$, $1s_b$, $2s_a$, $2s_b$, $2p_a{}^0$, $2p_b{}^0$, $2p_a{}^1$, $2p_b{}^1$, $2p_a{}^{-1}$, $2p_b{}^{-1}$ to build molecular orbitals in LCAO form, and configuration interaction calculation for normal as well as excited states. On this general background, they discussed various methods of approximation and gave the main results simple physical interpretations.

Among homopolar diatomic molecules of elements of the first period, Li_2 is obviously the simplest. Ishiguro *et al.* (19) studied this molecule in a manner similar to the study of O_2, and they went into more detail in some respects. The main features of these two papers will be briefly described in the following section.

Diatomic lithium.—Considering that the experimental data are only available for limited cases, they directed their attention to four states $(\sigma_g 2s)^2\ {}^1\Sigma_g{}^+$, $(\sigma_g 2s)(\pi_u 2p)^1\Pi_u$, $(\sigma_g 2s)(\sigma_u 2s)^3\Sigma_u{}^+$, ${}^1\Sigma_u{}^+$. They found that, for the first two states even the naive HL method gives lower total energy than SCF MO method. For the latter two states HL and ASMO give identical wave function. However, the description at this stage cannot be regarded as satisfactory even qualitatively. For instance, in this stage $(\sigma_g 2s)(\sigma_u 2s)\ {}^1\Sigma_u{}^+$ is purely ionic unlike other states, so that its energy is calculated to be too high for the same reason as Moffitt pointed out for the cases of O_2 and C_2H_4, and the order of excited levels of ${}^1\Sigma_u{}^+$ is not given correctly. If we take, however, all configurations ($\leqq 8$) into account and calculate their interaction, these difficulties are removed, and we can obtain remarkable improvement in excitation energy, depth of the adiabatic potential, difference between oscillator strengths calculated by the length method and by the velocity method, and so on. Further, the differences in the results calculated with the use of various values of orbital exponents are considerably reduced through configuration interaction, except particularly delicate quantities such as molecular quadrupole moment.

The characteristics of the wave functions obtained by CI calculation can be described as follows in comparison with those corresponding to simple ASMO. In the case of the normal state ${}^1\Sigma_g{}^+$, we obtain the transverse correlation which tends to keep two electrons apart on opposite sides with respect to the molecular axis, besides the longitudinal correlation describable in terms of semilocalization. In the state ${}^1\Sigma_u{}^+$, which is essentially ionic, both σ_g and σ_u are subject to strong sp hybridization and the charge due to σ_g is concentrated to the central part of the molecule while that due to σ_u is spread outwards; the situation resembles $1s\sigma 2p\sigma{}^1\Sigma_u{}^+$ of H_2 to some extent. In the state ${}^3\Sigma_u{}^+$, however, sp hybridization is small, and is hardly affected by CI. Finally in the state ${}^1\Pi_u$ we get a strong covalency character. The simple

description $\sigma_g \pi_u {}^1\Pi_u$ of this state may be considered to a certain extent similar to $\sigma_g \sigma_u {}^1\Sigma_u{}^+$ if we rotate the axis of reference by 90 degrees, so that it will give too much probability for two electrons being on the same side of the nodal plane of the orbital π_u. The lack of freedom for improving this point in our framework will be the main cause of rather poor results for this state $^1\Pi_u$.

Further they examined the validity of the approximation of neglecting the overlap between $1s$ orbital of one atom and $2s$, $2p$ orbitals of the other. This approximation corresponds to that which was employed by Löwdin in his treatment of metallic sodium. The increase in the dissociation energy due to this neglect of overlap is equal to 0.60 ev in the case of ASMO and to 1.33 ev in the case of HL method, which is even greater than the dissociation energy 1.06 ev itself. Still further they performed a series of calculations on the approximation of collapsing the $1s$ core to the nucleus. According to their results, various quantities, particularly the dissociation energy, are affected seriously by the restrictive conditions imposed on the valence electron wave functions.

Besides the studies by these authors, the lithium molecule was also investigated by Faulkner (20). He carried out the calculation of SCF LCAO MO for this molecule, varying the orbital exponents of $2s$ and $2p$ independently, and obtained for sp hybridization and molecular quadrupole moment results which are considerably different from those given by Kotani et al. The discrepancy, which seems to be too large to be attributed to the different choice of parameters, remains to be investigated.

In the case of O_2 molecule, it was found that the simple MO description is better than the simple HL picture, contrary to the situations for H_2 and Li_2 molecules, and that the π-electrons are more suitable to MO description than σ-electrons, which is rather unexpected. Analyzing the situation more generally, they concluded that the preference between MO and HL descriptions depends, not only on the degree of the overlap of orbitals, but also on the strength of the effective potential to which the electrons in question are subjected. They carried out the CI calculation for the normal state, taking into account all those fifteen configurations which directly combine with the main configuration, and found that the energy is lowered by 3.5 ev compared with SCF MO result. The electron spin density at the nucleus, which was derived experimentally from the hyperfine structure of the microwave spectrum of $^{17}O^{16}O$, vanishes in SCF MO approximation, but is given by CI calculation in good agreement with experiment. However, the molecular quadrupole moment and the longitudinal magnetic field due to electron spins at the nucleus

$$-2\mu_B \left\langle \sum_i \frac{P_2(\cos \theta_i)}{r_i{}^3} 2S_{iz} \right\rangle$$

are not much improved. They found that, analyzing the wave function obtained through CI calculation, the sp hybridization of the σ-bond, semilocalization in the π- and σ-bonds and the interatomic correlation between π-electrons and σ-electrons play important rôles in improving the value of the total energy and the wave function. Accordingly, for the excited states

the authors selected the configurations to be included in such a way that the features mentioned above can be incorporated in the calculation. This gives secular equations of dimensions $\leqq 5$ for the states under consideration. This configuration mixing improves the excitation energy and the oscillator strength fairly well, though not completely satisfactorily. Further, the $^3\Sigma_u^-$ state, which was particularly studied by Moffitt, is purely ionic in the naive MO description, but has been found to have a considerable covalency character through configuration mixing, and to show a strong interatomic correlation between π- and σ-electrons. This decreases the separation between $^3\Sigma_u^+$ and $^3\Sigma_u^-$ to 5.3 ev from its original value 9.8 ev in the simple ASMO, but is still larger than the observed value 2.2 ev. On the other hand, Ohno & Itoh (21) showed that the energies of these states can be improved without resorting to CI; they chose a different value of the orbital exponent for $^3\Sigma_u^-$, which is essentially ionic, from that for $^3\Sigma_u^+$, which is covalent. The calculation involves several approximations, but is of an essentially nonempirical nature. By this calculation, they succeeded in getting very satisfactory values for excitation energies, particularly for the separation of two levels $^3\Sigma_u^+$ and $^3\Sigma_u^-$. Kotani $et\ al.$ (18) suggested that such procedure will probably give satisfactory results also for

$$-2\mu_B \left\langle \sum_i \frac{P_2(\cos\theta_i)}{r_i^3} 2S_{is} \right\rangle$$

discussed above.

$BH\ molecule.$—Ohno (22) carried out exact nonempirical calculations of the normal and lower excited states of BH molecule, on HL method and SCF MO method, as well as MO CI method. The building bricks were $1s$, $2s$, $2p\sigma$, $2p\pi$ orbitals of B and $1s$ orbital of H, orbital exponents being chosen suitable to the neutral atoms. In CI calculation he took all the possible configurations subject to the restriction that $1s$ of B is always doubly occupied, and obtained considerable improvement on simple MO and VB pictures. In comparison with energy values of the triplet states, however, those of the singlet states and the dissociation energy of the normal state still are not satisfactory. He showed that this difficulty may be removed by taking different values of the orbital exponents for Be, Be$^+$, and Be$^-$.

$NH_3\ molecule.$—For this same molecule, LCAO SCF calculations have been made independently by Duncan (23) and by Kaplan (24). Duncan employed Slater orbitals while Kaplan used a Hartree Fock field for the nitrogen atom, otherwise the calculations run quite parallel. Calculations are exact, except for the neglect of higher terms in the expansion used for the evaluation of many-center integrals. The results are compared in Table II. According to this result, Slater orbitals are a little inferior to HF orbitals with respect to the dissociation energy, but are superior to the latter for most other properties. In particular, the calculated values of the dissociation energy agree remarkably well with experiments. This situation is similar to that in Ellison-Shull's investigation of the water molecule. Kaplan transformed his MO's into equivalent orbitals, and, under the restriction that

TABLE II

RESULTS OF SCF MO CALCULATIONS FOR THE AMMONIA MOLECULE

	Calculated		Observed
	Hartree-Fock	Slater	
total energy	−56.280 au	−56.096 au	−56.596 au
dissociation energy	10.3 ev	8.91 ev	12.47 ev
dipole moment	1.82 D	1.486 D	1.46 D
1st ionization pot	14.0 ev	9.94 ev	11.0 ev
2nd ionization pot	19.3 ev	16.20 ev	17.0 ev
hump energy	3.97 ev	—	0.25 ev
first excitation energy	too large	too large	—

two electrons are always present in each bond, performed a partial CI calculation. The gain in energy due to this restricted CI was only 0.3 ev.

UNITED ATOM ORBITALS

The main practical trouble of the LCAO MO method and the VB method, in which sets of atomic orbitals located at different centers are used as building bricks, lies in the difficulty of computing various molecular integrals of two, three, and four center types. Hence an alternative method deserves careful study, in which molecular orbitals, or the total molecular wave function itself, are constructed in terms of quasi-atomic orbitals around a single point suitably chosen in the molecule. This latter method works very favorably when the nuclei are close together, or when we deal with a highly excited electron, or when the arrangement of nuclei is highly symmetric. In cases of most molecules, however, one center expansion must contain terms with spherical harmonics of relatively high orders. The question is: whether it is advantageous to adopt the first method and to increase the numerical accuracy of molecular integrals or is it preferable to follow the second method and to increase the number of terms with higher harmonics. A few recent papers dealt with the development of the second method with the purpose of answering the above question. Funabashi & Magee (25) treated H_2, H_2O, and CH_4; Handler & Arnold (26) studied H_2 and H_3^+; Huzinaga (27) discussed H_2 and H_2^+, and Carter (28) and Koide, Sekiyama & Nagashima (29) calculated CH_4, by one center orbital method. The work by Koide, Sekiyama and Nagashima corrected and extended the early research by Massey, Buckingham & Tibbs (30), but the ratio (∼98 per cent) of calculated and observed total energies given by their method is lower than the same ratio (∼99 per cent) given by LCAO SCF MO method for, say, the NH_3 molecule. There seems to remain, however, much room for further development in this direction with the use of high speed automatic computing machines.

Free Electron Models

Long chains of conjugated double bonds, such as are realized in polyenes, cyanines, etc., still present puzzles to theoreticians. During 1957 several papers were published which dealt with this "classical" problem in the naive or improved free electron model.

Araki and Huzinaga (31) tried to explain the fact that the first absorption wavelength of an unsymmetric cyanine dye is shorter than the mean value of the first absorption wavelengths of two corresponding symmetric cyanines. By introducing a few parameters characteristic of each end group, they showed that the free electron model of MO type as well as the Herzfeld & Sklar model of VB type could account for the relation in question.

Araki and his collaborators (32) tried to refine the usual free electron model by introducing interelectronic interaction in the linear free electron model of Kuhn's type or to Platt's circular perimeter model for catacondensed hydrocarbons. The usual theory, which does not take the interelectronic interaction explicitly into account, has the advantage of being so simple and easy to handle that it can be applied to fairly complicated molecules. On the other hand it has the disadvantage of being incapable of removing the degeneracy between spin multiplets, and has to be regarded as a qualitative theory rather than a quantitative one. However, if we should introduce the Coulomb interaction between electrons in its actual form, its matrix elements would diverge, so that some sort of manipulation is necessary. For this purpose they used a certain kind of two-dimensional average of the three-dimensional Coulomb interaction in the linear free electron model, and a Coulomb potential modified by zero cut off at small distance in the circular perimeter model. Both these methods give fairly satisfactory results, though in the latter method some questions seem to remain as to the order of singlet and triplet states. Further Huzinaga (33) worked out a similar refinement for Platt's two-dimensional free electron model, but its application to naphthalene (or azulene) was not so satisfactory.

On the other hand, Frost & Leland (34) introduced one-dimensional negative δ-function type potentials in the free electron (network) model in order to account to some extent for the ionization potential, adiabatic electronic energy curve, etc., which cannot be dealt with in the original free electron theory. They showed that these properties for H_2 and aromatic hydrocarbons could be qualitatively explained on adjusting the strength of the δ-function. Instead of this δ-function, Barrow (35) used a one-dimensional square well potential. He applied his model to σ-bond, and was able to reproduce roughly its characteristic properties.

Further, Ham & Ruedenberg (36) tried to introduce the interelectronic repulsion and the potential due to core skeletons into Sherr-Ruedenberg's free electron network model (37). The interelectronic repulsion was treated in a way similar to Araki's method. They could correlate their theory closely with orthodox treatments by Pariser & Parr (38) and with Pople (39), by ex-

pressing the matrix elements of interelectronic repulsion and core potential in the form similar to that in the LCAO MO theory.

Finally, the problem of bond length alternation in a long linear conjugate double bond has attracted the interest of several authors in 1957. Polyenes, carotenoids, cyanine dyes are examples for such systems. As the number of conjugate double bonds n increases the first absorption wavelength gets longer, but in the case of polyenes and asymmetric cyanines the wavelength seems to converge to a finite limit whereas in the case of symmetric cyanines the wavelength seems to increase linearly with n. This experimental fact was explained by Kuhn (40) as follows: from the standpoint of the VB theory there exist two equivalent structures for symmetric cyanines, but only a single lowest one for polyenes and asymmetric cyanines. Hence in the former molecules all CC bonds become equivalent on account of resonance, while in the latter ones single and double bonds are localized due to the incomplete resonance, and the bond length alternates as in the butadiene. As a result of this the Hartree field for π-electrons in polyenes and asymmetric cyanines has the period of two bond lengths, and in the limit of $n \to \infty$ we get energy bands, one completely filled and the other empty, which are separated by a Brillouin gap of finite breadth, so that the wavelength of the absorption corresponding to the transition from the top of the filled band (valence band) to the bottom of the empty one (conduction band) converges to a finite value. On the other hand, Araki (41) explained this limiting absorption as the excitation of a collective mode similar to plasma oscillation.

In view of the generally accepted importance of collective motions in solids and atomic nuclei, his suggestion is of much interest for molecular scientists, but this explanation of the phenomena under consideration can hardly be regarded as established because it is not clearly understood why a similar absorption does not occur in the long symmetric cyanines. Kuhn's interpretation is not free from criticism. It attributes the bond alternation to an end effect, but it is difficult to understand that the situation at the ends regulates the bond length alternation throughout a very long chain. In fact, the naive Hückel MO theory suggests that the equalization of bonds will take place very rapidly as n increases. Explanations of this difficulty were given independently by Labhart (42), Ooshika (43), and Huzinaga & Hasino (44), who showed with the use of MO theory that the alternation takes place as a bulk effect, and not as an end effect. If the bond length alternation is actually a bulk effect it should also occur in long symmetric cyanines, but Labhart has shown, by semiempirical calculation, that in symmetric cyanines the alternation does not occur until n exceeds 30. From this standpoint experimental studies of the absorption by very long cyanines are very desirable.

THEORIES OF MOFFITT, ARAI, AND HURLEY

The total electronic energy of simple molecules obtained from nonempirical calculation agrees fairly well with the observed values; for instance, LCAO SCF MO method usually gives about 99 per cent of the true

energy. Since, however, the total electronic energy itself is a large quantity, the discrepancy of 1 per cent cannot be regarded as small, when we are interested, e.g., in the dissociation energy or in the lower excitation energy. For instance, the CI calculation of Kotani *et al.* gave the total energy as -4059 ev, which is higher than the experimental value -4092 ev by *ca.* 30 ev. This contains the major part of the correlation energy, which is extremely difficult to include in rigorous calculation. Because of this unavoidable discrepancy, some pure theoreticians are not willing to put much reliance on the nonempirical calculations in the present stage.

The correlation energy is always a hard nut to crack. From the standpoint of molecular physicists, however, it is not necessary to calculate it completely in the nonempirical scheme, because the main part of the correlation energy is due to the electrons in the inner cores and is essentially atomic in nature. From this point of view, our task is to find some formalism with which we can calculate various molecular properties such as dissociation and excitation energies from the knowledege of properties of free atoms, which we may simply take from observation. In this respect such theories must necessarily be semiempirical in nature. Theories of Moffitt, Arai, and Hurley belong to this category.

Moffitt (45) emphasized the importance of intra-atomic correlation energy in the calculation of excitation energies of the oxygen molecule. The assumption was that the atoms retain their characters of the free state, even in molecules and that the total electronic wave function reasonably well can be approximated by antisymmetrized products of exact wave functions of the constituent atoms. Then the energy matrix of the total electron system in molecule can be written in the form

$$H = \tfrac{1}{2}(\tilde{M}W + W\tilde{M}) + \tfrac{1}{2}(\tilde{V} + \tilde{V}^+), \qquad \text{VIII}$$

where M is the overlap matrix, W the diagonal matrix with atomic term values as eigenvalues, and V is the matrix of the interatomic interaction energy. It was considered that the interatomic matrices M and V are small and can be replaced by their "orbital approximations" $\tilde{M}$ and $\tilde{V}$, i.e., by their values computed with the use of wave functions built from atomic orbitals. It was thought, however, the intra-atomic energy was by no means small, and it was built from empirical spectroscopic term values of the free atoms. Moffitt's second formulation

$$H = \tilde{H} + \tfrac{1}{2}[\tilde{M}(W - \tilde{W}) + (W - \tilde{W})\tilde{M}] \qquad \text{IX}$$

is obtained from VIII by substituting for V the approximate relation

$$\tilde{V} = \tilde{H} - \tilde{M}\tilde{W}. \qquad \text{X}$$

Actually he calculated excitation energies of O_2 (45), C_2H_4 (46), and C_6H_6 (47) on this formalism, and, as is well-known, he could obtain results which showed a good agreement with experiments. This method is generally known as the "method of atoms in molecule"(AIM).

The method of atoms in molecule was later applied to the H_2 molecule, and it was found that the method was not free from the following difficulties:

(a) If we follow AIM faithfully, and, in particular, take the correct orbitals for H⁻ which extend much more diffusely than $1s$ orbitals of H, the total energy of the molecule is too high [Pauncz (48); Hurley (49)].

(b) If we take as the orbitals for H⁻ the same orbital as H, the calculated total energy is smaller than the observed value for a certain range of the internuclear distance (Pauncz, Hurley).

Further, Rahman (50) calculated Li_2 in Moffitt's scheme, but the result was disappointing on account of the difficulty (b).

In these circumstances, new methods were proposed independently by Arai (51) and Hurley (49) with the intention of improving Moffitt's method. First, from the defect (a) of AIM, they considered that the electronic wave functions of atoms were more or less deformed in molecules; accordingly they assumed "deformed atoms" in molecule and expected that the exact molecular wave function could be more closely approximated by antisymmetrized products of wave functions of such deformed atoms. Further they assumed that $\tilde{H}$, $\tilde{M}$, $\tilde{V}$ and $\tilde{W}$ in VIII and IX could be calculated in sufficiently good approximation with the use of deformed orbital wave functions, which were chosen in Slater's type in actual calculation. The exponents of these Slater-type orbitals should in principle be determined for each atomic state so as to make the total energy a minimum, but they expected fairly good results to be obtained with the choice of orbital exponent common to covalent and ionic structures. This simplifies the calculation considerably. Second, as regards the intra-atomic correlation energy, we should substitute for W in VIII or IX the "observed" values for deformed atoms, i.e. the estimated energies of deformed atoms in which the correlation is fully taken into account. The defect (b) of AIM is expected to be removed by this procedure. Arai's method of "deformed atoms in molecule" (DAIM) took account of this correlation using equation VIII, while Hurley based his method of "intra-atomic correlation correction" (ICC) on equation IX to treat the same effect.

Arai estimates the energy values W_d of deformed atoms by employing actual wave functions of (virtual) deformed atoms. This energy consists of a term containing the energy W_f of a free atom and a few correction terms, and Arai takes account of the correlation energy by adopting observed spectroscopic term values for the former, and evaluates the other terms by actual computation. Hurley assumes, on the other hand, the correlation energy involved in W_d to be the same as that involved in the energy W_f of the free atom; that is to say, he assumes that the correlation correction $W_d - \tilde{W}_d$ for the deformed atoms in IX is equal to the corresponding quantity for the free atom $W_f - \tilde{W}_f$. This assumption makes the calculation by the method ICC much easier in comparison with that by DAIM method. We should note, however, concerning ICC method that the validity of the relation X, on which its formulation has been based, is open to some question in the case when atoms are deformed in molecules. An attempt to justify IX directly without the use of X has actually been made by Hurley himself (52).

The dissociation energies (in ev) obtained by applying these methods to the ground states of simple molecules are shown in Table III:

TABLE III

DISSOCIATION ENERGIES (IN EV) GIVEN BY THE METHODS AIM, DAIM AND ICC

	H_2	Li_2	N_2	FH	BH
orbital calculation with CI	4.26	0.77	3.29	1.96	2.22
AIM	4.35	41.0	15	8.33	—
DAIM	4.58	0.95	—	—	—
ICC	4.72	—	9.18	5.84	2.72
observed	4.74	1.05	9.91	6.08	<3.66

From this table it seems that both the methods ICC and DAIM are fairly successful for the ground states of these molecules. Further, the electric dipole moment of FH has been calculated by ICC method to be 2.33 D, which agrees with the experimental value 1.91 D better than the values given by the orbital approximation 0.93 and by AIM 3.01. Arai & Mannari (53) applied the DAIM method to the calculation of the nuclear quadrupole coupling constant q at a lithium nucleus in Li_2, and obtained the result which agrees qualitatively with the theoretical prediction of nuclear quadrupole moment from the shell model.

In applying ICC and DAIM methods we have to know the empirical values of energy levels of negative ions, which are not available. Arai & Onishi (54) proposed a method for estimating these values and applied it to the negative ion of Li. They assume that the total correlation energy of Li^- is a sum of correlation energies in $(1s)^2$, in $(2s)^2$ and that between $1s$ and $2s$. They identify the first and the last quantities to the corresponding ones in Li and Li^+, and estimate the correlation energy in $(2s)^2$ through extrapolation from Be, B^+, C^{++}, ... Estimation of energies of valence states for which no experimental values are available was also made by Hurley (55). He expressed the energies of known valence states in orbital approximation in terms of Coulomb integrals, exchange integrals etc., determined their values from empirical data, and estimated unknown valence-state energies with the use of them (e.g., for the ions of N).

Bingel (56) proposed a new method of treating the correlation energy in molecules. He expands the molecular wave function in terms of those of the united atom, and tries to take account of the correlation energy by using the observed spectroscopic data of the united atom. In this method the actual numerical calculation is required only for one-electron integrals, so that the labor of computation seems to be much reduced, but actually the convergence will be very slow—sometimes too slow for this method to be of any practical use. More recently Preuss (57) has conceived a method of calculation which is a combination of Bingel's method and AIM method. He introduces a parameter $p(R)$ which depends on the internuclear distance R

into the Hamiltonian and the wave function in such a way that at $R \to 0$ they reduce to Bingel's theory while at $R \to \infty$ they conform to AIM, and he determines $p(R)$ by the variation of energy. His results for H_2 and H_2^+ look very promising, but it is not clear whether his theory as well as Bingel's will work usefully for treating larger molecules.

Development of semiempirical π-electron theory.—The π-electron theory is a large, well-explored branch of quantum chemistry, where a vast deal of useful information has been derived from theoretical studies. In the early days of the theory, Hückel's MO's were exclusively used, and the energy of the total system was assumed to be given by the sum of energies of occupied orbitals. According to the more recent formulations of theory, one starts from the complete π-electron Hamiltonian in which the interelectronic Coulomb repulsion is included in the explicit form $\Sigma_{i<j} e^2/r_{ij}$. In the present stage of the theory, however, purely theoretical, nonempirical approaches can hardly give such details of the energy levels as are required by chemists, so that we have to resort to more or less semiempirical formulations of the theory. From this viewpoint, theories of Pariser & Parr, of Pople, and of McWeeny deserve particular attention.

In their first paper Pariser and Parr (38) succeeded in demonstrating how considerably the labor of nonempirical calculation of LCAO MO for C_6H_6 could be reduced through the introduction of a set of sensible simplifying assumptions. First of all, the neglect of differential overlap makes it possible to dispense with a great variety of cumbersome two-electron integrals, and leaves us only a small number of Coulomb integrals, which are rather easy to deal with. Moreover, they showed that even the model of two contacting spheres for the charge distribution of an atomic $p\pi$ orbital could give fairly good values for two center Coulomb integrals. However, as mentioned above, the purely nonempirical approach cannot be expected to give fruitful results which satisfy chemists. Pariser and Parr directed their efforts towards expressing such integrals as $\alpha, \beta, (1\ 1\ |\ 1\ 1)$ etc. in terms of several quantities which bear direct physical (chemical) meanings and replaced them by the corresponding empirical values. By this procedure, they hoped that the troublesome problem such as that of correlation between π- and σ-electrons could be swept out.

The method of Pariser & Parr has been applied widely by many authors.

Pariser himself (58) made a systematic study of structures of the polyacenes and of alternant hydrocarbons. Benzene was taken as the reference molecule and the values of β (resonance integral), $(1\ 1\ |\ 1\ 1)$ and $(1\ 1\ |\ 2\ 2)$ have been adjusted so as to give three benzene states $^1B_{1u}$, $^1B_{2u}$ and $^3B_{1u}$ correctly. Other Coulomb integrals, such as $(1\ 1\ |\ 3\ 3)$, were calculated theoretically using Slater atomic orbitals (AOs). It is remarkable to notice that the calculated spectra of the polyacenes using these values agree well with experiments.

Azulene, a polar molecule, was studied also by the same author (59). The results for the π-electron dipole moment are as follows:

SCF MO	1.7 D,
Perimeter MO+CI	3.36 D,
Hückel MO+CI	1.88 D,
Experiment	1.0 D.

Thus Hückel MOs give considerably better results than perimeter MOs. Some examples of the application of the method are:

> Melamine, by Dewar & Paoloni (60),
> Carbonyl group, by Sidman (61),
> Triarylmethyl radicals, by Murrell (62),
> Diphenyl, by Iguchi (63).

Pople (39) also employed the same sort of simplified procedure as Pariser & Parr for the determination of the SCF MO for conjugated molecules. Mc-Weeny & Peacock (64) studied nitrogen heterobenzene modifying the semi-empirical SCF MO method proposed for hydrocarbons by Pople.

These authors have shown that their theories can be brought into forms closely resembling the old Hückel theory, and they have actually given the procedure on how to derive the values of these parameters from more fundamental or empirical quantities. With this choice of parameters α and β the Hückel MOs turn out, of course, to be very similar to SCF MOs.

To treat the ground state and the first few excited states of heterocyclic systems, by admitting limited configuration interaction, there are various possibilities for choosing starting orbitals, which range from Hückel MO of the parent hydrocarbon to SCF MO of the substituted system.

Taking pyridine and pyrazine as examples, McWeeny (65) summarized relative merits of seven different choices of orbitals. The simplest possible treatment, based on the Hückel orbitals for the hydrocarbon, gives generally a surprizingly good approximation to the results obtained using the SCF MO of the nitrogen derivatives (which are assumed to be rather accurate). But the closer examination of the results shows that in the case of pyrazine the Hückel orbital of benzene does not give as good results as in the case of pyridine. In the case of pyrazine the possibility of improving the ground state by mixing with the chosen excited configurations is excluded by a direct consequence of the high symmetry of the molecule. In this case it is necessary to modify the Hückel orbitals of benzene to a high degree of precision, namely, it is necessary to introduce SCF MO for the perturbed system. Another conclusion is that the SCF MO of the actual (perturbed) system gives extremely satisfactory results for the first few excited states, even if the CI is confined to degenerate or near-degenerate functions.

Howe & Goldstein (66) used a new value for β_{C-Cl}, resonance integral between C and Cl, which was determined by nuclear quadrupole coupling, to treat the electron distribution and energy levels in chlorobenzene. Butadiene has been studied by Fain & Matsen (67), and by Berry (68). Higuchi (69) treated allyl radical, a three π-electrons system, as one of the simplest examples of radicals. Aihara & Niira (70) calculated some lower excited levels

of benzene using the bond orbital formalism. A general theory of inductive substitution effects and mesomeric effects in alternant hydrocarbons has been given by Goodman, Ross & Shull (71).

MOLECULAR QUANTITIES

Nuclear quadrupole coupling constant,[3] *q.*—Q of the ground state of Li_2 was predicted positive from the experimental value of *eqQ* and the nuclear quadrupole moment Q (72) calculated on the basis of the nuclear shell model; for example, it was estimated as 0.016 au by Sternheimer & Foley (73).

On the other hand, several attempts were made to determine this quantity nonempirically from the knowledge of the electronic structure of the molecule. The results of q and the corresponding Q hitherto obtained are summarized in Table IV.

TABLE IV

VALUES OF q FOR Li_2 AND OF Q OF ^7Li NUCLEUS

q (au)	$Q \times 10^9$ (au)
-0.0070 calc. with pure HL wavefunction	1.3 derived from q
-0.0066 calc. with simple ASMO wavefunction	1.4 derived from q
0.0018 calc. with James' function	-5.1 derived from q
0.0021 calc. with James' function (including the effect of core polarization)	-4.3 derived from q
-0.0028 calc. with MO CI wavefunction (Ishiguro *et al.*)	3.3 derived from q
0.0068 calc. with DAIM wavefunction (Arai *et al.*)	-1.3 derived from q
0.016 derived from Q	-0.6 estimated from nuclear shell model

Recently, Ishiguro *et al.* (19) calculated q of this molecule by using their CI wave function and obtained a negative value of a very small magnitude, -0.0028 au. The difference of this result from the previous ones (73), (74) obtained by using the James' function, is due, partly to the shortage of longitudinal correlation described by Ishiguro's function, and partly to the lack of π-character in James' function.

Arai & Mannari (53) obtained a positive and fairly large value of q,

[3]

$$q = 2e \left\langle \sum_i \frac{1}{r_i^3} P_2(\cos \theta_i) \right\rangle,$$

$$m_z^s = -2\mu_B \left\langle \sum_i \frac{1}{r_i^3} P_2(\cos \theta_i) 2S_{iz} \right\rangle,$$

$$\rho_{spin}(0) = \left\langle \sum_i \delta(\vec{r}_i) 2S_{zi} \right\rangle_{S_z = S}.$$

Gradient of electric field at a nucleus.

0.0068 au, using the wave function given by DAIM method in which the degree of sp hybridization is unexpectedly large.

Das (75), assuming a localized MO with sp hybridization for the BC bond in the $B(CH_3)_3$ molecule, calculated the value of q at the nucleus B. He obtained 0.460 au for q, which is smaller than the experimental value, 0.596 au. The disagreement is in the same direction as that between the calculated values and the predicted one from the nuclear shell model for the Li_2 case. A better result, 0.585 au was obtained by Townes' & Dailey's method, though it is admittedly crude.

Longitudinal magnetic field due to electron spin at the position of the nucleus,[3] *m.*—From an approach of HL type, Miller, Townes & Kotani (76) gave an estimate of this quantity for the ground state of O_2. They found that the discrepancy of their estimate from experiment remains about 15 per cent even if one includes the overlapping effect of π-orbitals. The remaining part was regarded as arising from molecular formation.

Kotani *et al.* (18) performed the calculation of this quantity by using their CI wave functions, and they found that even a fairly large number of CI could not take into account the effect of molecular formation on this quantity, as long as one employs atomic orbitals (AOs) with the same orbital exponents as the neutral atom. They showed that an explanation for this discrepancy could be given by the assumption of contraction of atomic orbitals of O^+ in ionic structures.

Electron spin density at the position of the nucleus,[3] $\rho_{spin}(0)$.—Abragam *et al.* (77) calculated $\rho_{spin}(0)$ for the free Mn^{++} ion using the CI wave function, and obtained about 10 per cent of the experimental value in the case of complex salts. Unfortunately, their form of the variational function was not flexible enough, particularly it could not include the polarization of inner s electrons.

Then, Wood & Pratt (78) estimated this quantity by using the unrestricted Hartree-Fock (HF) orbitals which were obtained for Fe with the approximate method of averaged exchange potential proposed by Slater (79). They showed that the contributions to $\rho_{spin}(0)$ from $(1s)$ and $(2s)$ electrons are both negative and have a comparable order of magnitude with that of the positive contribution from $(3s)$ electrons, and that the total $\rho_{spin}(0)$ amounts to about 80 per cent of the above experiment. Heine (80) independently performed a similar calculation and found a qualitatively analogous result to those of the above authors, although he used the HF field of Cu^+ to calculate the unrestricted HF orbitals for Mn^{++} and neglected

[3]

$$q = 2e \left\langle \sum_i \frac{1}{r_i^3} P_2(\cos \theta_i) \right\rangle,$$

$$m = 2\mu_B \left\langle \sum_i \frac{1}{r_i^3} P_2(\cos \theta_i) 2S_{iz} \right\rangle,$$

$$\rho_{spin}(0) = \left\langle \sum_i \delta(\vec{r}_i)^2 S_{zi} \right\rangle_{S_z=S}.$$

Gradient of electric field at a nucleus.

the polarization of (1s) electrons. Further he calculated the unrestricted HF (4s) orbitals and found that the contribution from (4s) electrons is positive and almost cancels the value of $\rho_{spin}(0)$ obtained above for Mn^{++}. This result might explain the experimental evidence that $\rho_{spin}(0)$ of the neutral Mn atom in complex salts is nearly zero. The relative behavior of $\rho_{spin}(0)$ for Cu^{++} and Cu found by experiment, however, is opposed to this tendency, and it could not be explained by his procedure alone. The wave functions adopted in the preceding two papers are single Slater determinants, which do not have the correct symmetry of the ion, ^6S. They thought, however, that this defect may have little influence on the final result.

For the ground state $^3\Sigma_g^-$ of O$_2$, Kotani *et al.* calculated this quantity by using their 15-dimensional CI wave function, and obtained the result in good agreement with experiment. Most of this magnitude, however, can be considered to come from an angular exchange polarization of σ_u (2s) electrons in the neighborhood of the oxygen nucleus under consideration, contrary to the case of Mn^{++} where Wood and others had considered the radial exchange polarization of (ns) electrons. It must be noted that for O$_2$ $\rho_{spin}(0)$ can be obtained in good agreement with the experiment, without taking the polarization of inner core electrons into consideration.

Mizushima (81) obtained the formulas for the magnetic hyperfine structure, hfs, valid for the Hund case a in linear molecules and applied them to the analysis of hfs of NO. Considering the small experimental value of the dipole moment (0.16~0.8 D), he constructed the wave function from only neutral structures whose weights were determined with the use of the observed data about hfs and fs of this molecule. Moreover, he estimated $\rho_{spin}(0)$ at the N nucleus by mixing with the above wave function all the structures arising from one electron excitation $2s \rightarrow 3s$. In this way he could obtain about 50 per cent of the experimental value of $\rho_{spin}(0)$. His procedure, however, corresponds to the radial exchange polarization contrary to the O$_2$ case.

Molecular dipole moment.—Das (75) intended to use as a bond orbital a localized MO, as already stated in the case of q. He considered two methods to calculate the dipole moment of the BH$_3$ part in a BH$_3$CO molecule. On the one hand, he assumed localized MOs for BC and BH bonds and utilized some information on the CO molecule for the CO bond. He determined the ionic character of the BC bond so that the q at B may agree with the experiment. Using this ionic character for a BC bond he determined the dipole moment of BH$_3$, as -0.09 au, so that the total dipole moment of BH$_3$CO may coincide with experiment. On the other hand, he directly calculated the same quantity assuming localized MOs for BH bonds, and obtained -0.83 au for the dipole moment. The inconsistency of these two results may be ascribed to the assumptions of using localized MOs and of using undistorted AOs as building-bricks for these MOs. Which of the two assumptions is the main cause of this discrepancy, however, was left unanswered in his paper.

Molecular quadrupole moment, Q_{mol}.—As has been already mentioned (18), Q_{mol} of O$_2$ decreases algebraically as sp hybridization increases; for example, it is -1.533 au by their 15-dimensional CI, while it is 0.152 au

by the simple ASMO. Although the calculated values of Q_{mol} with sp hybridization are too large in magnitude compared with the experiment, $|Q_{mol}| < 0.82$ au, they are still smaller than the one calculated by Scherr (82) for N_2. Greenhow & Smith (83) intended to show that for O_2 a smaller positive value for Q_{mol} was compatible with a reasonable amount of sp hybridization, but they had thereby neglected the overlapping effect between $(2s)_a$ and $(2p\sigma)_b$ orbitals. Actually, this effect is very large.

For Li_2 the introduction of sp hybridization increases Q_{mol} contrary to the case of O_2, for example, 8.72 au by the simple ASMO, and 19.46 au by their best CI.

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SURFACE CHEMISTRY AND CONTACT CATALYSIS[1]

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The present review deviates from previous reviews inasmuch as it deals mainly with contact catalysis since adsorption phenomena are treated elsewhere in this volume.

While the year 1957 failed to bring forth a "break-through" in the understanding of contact catalysis, it was a fruitful year for catalysis research, with the main emphasis on problems related to industrial catalysts and catalytic reactions.

The third edition of Griffith's *Contact Catalysis* (1) and the fifth volume of *Catalysis*, edited by Emmett (2), were published. The latter contains chapters on hydrogenation, oxo-synthesis, hydrocracking, hydrodesulfurization, and hydrogen isotope exchange.

The papers and discussion of the International Congress on Catalysis, held in September 1956, appeared as Volume IX of *Advances of Catalysis* (3). This volume consists of 83 papers, including reviews on magnetic studies concerned with the determination of the structure of catalysts [Selwood (4)], structure and texture of catalysts [de Boer (5)], electron transfer and catalysis [Garner (6)], role of catalysis in corrosion processes [Uhlig (7)], catalytic technology in the petroleum industry [Oblad, Shalit & Tadd (8)], the relationship between homogeneous metal carbonyl reactions and heterogeneous catalysis [Wender & Sternberg (9)], tracer and adsorption techniques [Emmett (10)], testing of heterogeneous catalysts [Dowden & Bridger (11)], and the catalytic action of semiconductors [Wolkenstein (12)].

Other reviews published in 1957 covered the relationship between catalysis and chemisorption (13), semiconductivity (14), and stereochemistry (15). The preparation of catalysts was the subject of a symposium held by the Division of Petroleum Chemistry at the 129th (Dallas) Meeting of the American Chemical Society in 1956. The papers (16 to 16i) covered principles and techniques of preparing catalysts and the factors in catalyst preparation that influence activity, selectivity, and stability.

Catalysts and their physical and chemical properties.—The intensive study of catalyst activity in relation to their physical and chemical properties was continued. Major effort was devoted to catalysts having industrial significance, particularly in petroleum technology.

[1] The survey of literature pertaining to this review was concluded December, 1957.

Silica-alumina cracking catalysts, representing the largest volume of commercial catalysts, received particular attention. Attempts to correlate catalytic activity with electrical properties, crystal structure, crystal size, dislocations, and methods of preparation were continued. Examples for these studies follow.

On the basis of results of differential thermal analysis, x-ray studies, and catalytic evaluation of very pure silica-alumina specimens of varying composition, Gray (17) suggests that the active species is a half-inverted spinel with the protons in certain octahedral sites. The same spinel is thought to be responsible for the formation of mullite at much lower temperature and may be considered as the incipient mullite phase. The surface acidity of fresh silica-alumina cracking catalysts was estimated by Richardson & Benson (18) from the quantities of permanently bound basic gas (pyridine, trimethylamine) adsorbed at 20° to 30°C. The permanently bound gas was assumed to be the portion of adsorbed gas which desorbed very slowly and was determined by a quartz helix balance. The acidity was found to depend on particle size, traces of water present in the catalyst and, to some extent, on temperature. The acidic sites were partially of the Bronsted type, as indicated by the effect of traces of water, and covered not more than a few per cent of the total surface area (400 m.^{2}/gm.).

Benesi continued his studies (19) of the acidity of clay, cracking catalysts and various acids mounted on silica gel. The acidities were determined by titration with n-butylamine in benzene suspension using adsorbed Hammett indicators. In the case of mounted acids, the strength and proportion of titratable acid depended on the surface concentration. With clays, the acidity measurements made it possible to differentiate between clay types, the kaolinite acid centers being stronger than those of attapulgite or montmorillonite. Among the cracking catalysts silica-alumina and sulfur-resistant clay (Filtrol) had exceedingly strong acid centers, while the silica-magnesia centers were very weak.

According to Webb (20), the number of acidic sites on alumina remains unaffected by treatment with hydrofluoric acid. This is shown by the constancy of the amount of chemisorbed ammonia on hydrogen fluoride treated alumina. However, the difficulty of removing such ammonia increases with the extent of hydrogen fluoride treatment, indicating increase in acid strength. The first 0.5 per cent of added hydrofluoric acid is the most effective and appears to remain on the surface, influencing the acid sites in proportion to the surface area covered. When a sufficient amount of acid is added to affect the entire surface, the expected effect is not realized fully and a large portion of the acid reacts with the alumina and forms crystallites of basic aluminum fluoride.

According to Schlaffer, Morgan & Wilson (21), in the aging of silica-alumina exposed to elevated temperature (478°–950°C.) and steam (up to 7 atm.) the specific surface area, S, decreases with time, t, according to the formula $-dS/dt = kS^n$; k and n ($= 4$ to 10), being dependent on temperature and steam pressure. At the highest temperatures the rate of change in the

specific pore volume during aging was proportional to the rate of change of the specific surface area but was smaller at lower temperatures. Based on this work and electron microscope studies of Adams & Voge (22), the following picture can be made of the aging process. The unaged silica-alumina gel consists of coherent aggregates of smooth spherical particles of about 45 A in diameter with a relatively narrow distribution. The specific surface area is the geometrical area of these particles and the pore volume is the void-volume resulting from packing together these particles. The first step in aging is the formation of fillets between particles by the deposition of material in the region of contact. At this stage, surface area and pore volume are not much changed, but bridges are provided for subsequent material transport by surface migration, volume diffusion, and viscous flow, each of these mechanisms having different activation energies. Surface migration occurs at low temperatures, and increases the pore diameter but does not change the pore volume, since the relative position of the particles remains unchanged. At temperatures below 800°C. in the presence of steam, the decrease in the surface area can be accounted for quantitatively by the increase in particle diameter with widening distribution. At high temperature, volume transport (coalescence) comes into play, accompanied by decrease in the pore volume but not in the pore diameter. High values of $n(>5)$ observed in the presence of steam are not compatible with diffusion and are ascribed to the formation of a volatile species, $Si(OH)_4$.

Franklin & Nicholson (23) found that the activation energy for the decomposition of isobutane, 30.5 kg. cal./mole. remained constant for heat and steam sintered silica-alumina catalysts of various surface area (80 to 300 m.²/gm. Also, a linear relationship was observed between the logarithm of the frequency factor and the activation energy for the decomposition of all hydrocarbons obeying first order kinetics.

McEvoy, Milliken & Mills (24) have studied the penetration of metal contaminants contained in certain crude oils into pelleted cracking catalysts during the cracking process. The metals were found to be deposited preferentially on peripheral layers of the catalyst pellets. In one example, 40 to 60 per cent of the deposited metal settled on the outer 35 micron layer of 4 mm. pellets. In moving bed cracking operation this outermost layer, and with it the major portion of the metal contaminants, is removed by rubbing attrition.

The mechanism of semiconductor catalysis was discussed by Hauffe (25) in terms of his "Baender" model, and was applied to the catalytic decomposition of nitrous oxide and ozone on oxides by Hauffe & Schlosser (26).

According to Wolkenstein (27), the semiconducting catalyst can be visualized as a giant polyradical, the free valencies of which are due to the equilibrium between the electron-hole pairs. On approaching the semiconductor surface a molecule may attract the free conduction electrons in such a way that these become localized near one of its atoms, whereby the bond in the molecule is eventually broken and a new bond between the surface and the atom is established.

Weller & Voltz (28) studied the electrical resistance of chromic oxide as a function of the oxidation-reduction state of the surface. The resistivity of oxidized chromia at 500°C. was found to vary inversely with the 1.2 power of the total excess oxygen chemisorbed and to reach a maximum with increasing hydrogen pressure. Exposure of the reduced oxide to water vapor in hydrogen caused a reversible increase in the resistivity and hydrogen evolution. These results were explained by the formation of chromous oxide on the surface and by the behavior of chromic oxide as an n-type semiconductor in dry hydrogen. Wagner's elementary treatment of the relationship between resistivity and oxygen pressure was found to be inapplicable in this case because of the large deviation of stoichiometry.

Bielánski, Derén & Haber (29) compared the electric conductivity and the catalytic activity of the n-type (zinc oxide and ferric oxide) and of p-type (chromia and magnesia) semiconductors and of their mixtures. The reaction studied was the dehydrogenation of ethanol. In the temperature range 300° to 700°C., the conductivity of n-type semiconductors increased while that of the p-type semiconductors decreased. The anomalous behavior of chromia above 450°C. was ascribed to a p→n-type transition. The catalytic yield was found to be related to the change in the conductivity.

The formation of an oxide film and of copper powder on the *111* face of copper single crystals during the catalytic reaction of hydrogen and oxygen was the subject of studies by Cunningham & Young (30). The surface of the *111* face was examined by elliptically polarized light while the reaction was in progress at 325° to 425°C. and at oxygen content of 0 to 17 per cent. Below 5 per cent oxygen no oxide film was detectable, while above this concentration oxide films of up to 75 A thickness were formed. In the absence of the oxide film the reaction rate was independent of the oxygen concentration, but on the oxide coated catalyst the rate increased with the oxygen concentration. In the presence of the oxide film, a dendritic growth of copper powder occurred over a period of several hours at imperfections resulting from the polishing of the surface. With increasing area of the powder the rate of the reaction also increased. At conditions under which no oxide formed, the copper powder slowly disappeared and rejoined the single crystal lattice. Simultaneously the reaction rate between hydrogen and oxygen decreased. The powder could not be removed by heating in hydrogen alone, even at 500°C. These observations give a good example of a significant increase and decrease in the catalytic surface area with only minor changes in conditions.

By diffraction experiments with electron beams of different penetrations, Yamaguchi, and Yamaguchi & Takeuchi (31, 31a) determined the distribution of the minor components in promoted and mixed nickel catalysts. The powder of reduced copper containing 1 mole per cent of magnesia (or nickel oxide) gave diffraction patterns with 50 kv. electrons, showing on the surface of the catalyst a predominance of the oxide structure over copper, the

catalyst substrate phase. With more penetrating electrons (at 200 kv.), the diffraction pattern for copper became stronger than that for the oxide, showing the expected copper to oxide ratio. Similar observations were made on a reduced copper-nickel catalyst containing 10 per cent nickel. The outer surface was found to contain nickel-rich mixed crystals besides nickel and copper crystals, while the inside of the crystal grain contained copper and copper-rich crystals.

According to x-ray diffraction studies of Davis, Griffith & Marsh (32) coprecipitated chromia-alumina catalysts are inhomogeneous if they contain 14 to 45 per cent chromia. The alumina-rich fraction contained boehmite and bayerite. Above 50 per cent chromia, only η-alumina and η-chromia were found after heating in air at 500°C.; the gels yielded products containing solid solutions of the α-oxides and of the η-oxides.

Cogelled molybdena-alumina, an outstanding reforming catalyst for virgin naphtha, was subjected to an exhaustive physico-chemical study by John *et al.* (33). The authors concluded that a stable nonstoichiometric molybdous oxide was the active component of the catalyst.

Rowlinson & Cvetanović (34) studied the effect of adding oxides of similar cation radius but different valency on the dehydrogenation activity of the oxides of zinc, iron, and nickel.

The effect of the size of catalyst granules on the hydrogenation of benzene was investigated by Burke & co-workers (35) using nickel and nickel oxide supported on silica gel of 20 to 200 mesh size as the catalyst. On increasing the subdivision the velocity constant was found to be proportional to the external surface area down to a critical granule size. Further subdivision below this critical size had no effect on catalytic activity, since, on reaching the critical size, sufficient area was exposed to allow the adsorption of all of the catalysts on the surface of the carrier. The decrease in catalytic activity with increasing particle size was ascribed to the blocking of active sites in larger pores by the condensation of benzene.

Cratty & Granato (36) suggest that the dependence of the catalytic activity of nickel foils on deformation and annealing is due to dislocations serving as active sites in heterogeneous catalysis. To verify this suggestion it is proposed to correlate catalytic activity with dislocation density which can be determined by etch-pit counting and by measuring the broadening of the x-ray line width.

Several papers dealt with the preparation of catalysts. According to Aller (37), the catalytic activity of Raney type cobalt catalyst, prepared by treating fine mesh cobalt-aluminum alloy powder with alkali, depends on the aluminum content of the finished catalyst. Aluminum removal was found to be much more complete with cobalt than with nickel. Thus, for example, at 100°C. at certain conditions of alkali treatment 8 to 9 per cent aluminum was left in the nickel catalyst while the aluminum content of the corresponding cobalt catalyst was reduced to 0.07 per cent. Extensive removal of the

aluminum leads to the collapse of the skeletal structure and thereby yields inactive catalysts. The preparation of Raney iron in the form of fine powder was described by Johnston, Heikes & Petrolo (38).

Solid catalysts used for the polymerization of ethylene and covered by extensive patent literature were discussed by Peters, Zletz & Evering (39) and Field & Feller (40). Nickel-charcoal and molybdena-alumina were found to be active if used in the reduced state. A further improvement in the activity (polyethylene yield) was effected by the addition of small amounts of such promoters as sodium, calcium hydride or lithium aluminum hydride. These promoters have a threefold function. They reduce the catalyst, as shown by their activating effect on unreduced catalysts. The promoters also act as scavengers by reacting with electron rich catalyst poisons such as water, hydrogen sulfide and carbon dioxide. Since the promoters give improved polymer yields, even in the absence of catalyst poisons and of a solvent under conditions at which the interaction with the catalyst is minimized, it appears that they also react with ethylene itself.

Ortho-parahydrogen conversion and hydrogen-isotope exchange.—The interest in the ortho-parahydrogen conversion and hydrogen-deuterium exchange reaction continues unabated. This type of reaction was studied from the point of view of elucidating the reaction mechanism, and was also used as a diagnostic test for evaluating catalyst activity. The hydrogen isotope exchange reaction covered the hydrogen-deuterium reaction and deuterium exchange reactions with a great variety of hydrocarbons and also with acetone.

Chapin & Johnston (41) measured the rate of the surface catalyzed ortho-parahydrogen conversion at 5 to 100 atm. and 55° to 195°K., using chromia on alumina catalysts containing 0.05 to 2.47 per cent chromia. At low chromia contents the half life time of the conversion was proportional to the pressure and inversely proportional to the chromia content of the catalyst. At high pressure (high coverage) the temperature coefficient of the rate was positive, in contrast to the negative temperature coefficient observed at low coverage. These observations are in agreement with a conversion of physically adsorbed hydrogen molecules under the influence of the paramagnetic surface.

A highly effective hydrous ferric oxide ortho-para conversion catalyst has found an interesting practical use in connection with the liquefaction of hydrogen (42). Because of the high activity of the catalyst a rather small size converter suffices to produce liquid parahydrogen, which then keeps better since the evaporation caused by the heat released in the gradual conversion of liquid normal hydrogen into the para form is eliminated.

From the study of the catalytic activity of thirteen oxides for the hydrogen-deuterium exchange, it is concluded by Dowden, Mackenzie & Trapnell (43) that the activity is primarily determined by the electronic configuration of the metal ion, the highest activity being shown by ions possessing some, but not too many, unpaired d-electrons. The peaks of activity are

shown by the favorable configuration $3d^3$ (Cr_2O_3), $3d^7$(Co_3O_4) and $3d^8$(NiO) occurring just after the beginning and at the end of the period. If the metal ions possess few or no such electrons, the activity is low (TiO_2, V_2O_5, V_2O_3, CuO, Cu_2O, ZnO, Ga_2O_3, GeO_2) and the same is true for ions having excessive numbers of unpaired electrons (Fe_2O_3, MaO).

Svadlenak & Scott (44) sought to establish a correlation between the magnetic properties of various ferric oxides and ferrites and their catalytic activity for the low-temperature ortho-parahydrogen conversion. To this end γ-ferric oxide, α-ferric oxide, and a series of iron oxide-zinc oxide mixtures heated to elevated temperatures to form a varying degree of zinc ferrite were tested at $-195°C$. The catalytic activity decreased in the order: γ-ferric oxide, α-ferric oxide, mixed catalysts heated to temperatures below 500°C. Mixtures heated above 500°C. were found to be the least active and to have undergone a change in the magnetic susceptibility. The observations lead to the conclusion that the ferromagnetic structure is connected with the highest catalytic activity and that the antiferromagnetic structure shows more activity than the paramagnetic structure even if the latter contains some ferromagnetism.

Taylor & Kohn (45) found that the activity of dehydrated γ-alumina for catalyzing the hydrogen-deuterium exchange reaction increased seven-fold by irradiation with a Co^{60} source for thirty minutes. However, the activation disappeared after two to four days standing at room temperature. Less active catalysts showed a several thousandfold increase in activity but the enhancement lasted only a few hours. The observed effect was ascribed to electrons or positive holes trapped in special sites in the alumina lattice.

Voltz (46) investigated the catalytic effects of supported-base catalysts. Sodium dispersed on dried alumina showed no increased activity for the hydrogen-deuterium exchange reaction. However, on hydriding, a striking activation occurred yielding activity even at $-195°C$. Sodium dispersed on silica was less efficient than on alumina. Supported sodium and lithium catalyzed also the hydrogenation of ethylene, but for this reaction the hydriding had relatively minor effect. The supported catalysts showed higher activity than the corresponding hydrides, probably on account of their larger surface areas. It was suggested that the activation occurs on metal sites at metal-hydride interfaces. Hydrogen activation is thought to occur more readily on lithium than on sodium sites, while the reverse situation appears to be likely for the activation of ethylene.

According to Wright, Weller & Mills (47), the hydrogen-deuterium exchange is catalyzed by aluminum chloride at 10 atm. and 200°C. even in the absence of an organic co-catalyst. The reaction mechanism is thought to involve a heterolytic scission of the hydrogen molecules and an exchange with a hydrogen donor in the catalyst, the hydrogen donor originating almost certainly in water picked up by the aluminum chloride according to

$$D^+:D^- + H^+[AlCl_3(OH)]^- \rightleftarrows DH + D^+[AlCl_3(OH)]^-.$$
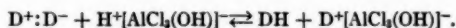
Significant exchange also occurred when a deuterium-iso-butane mixture was charged. In this case the reaction suggested involves the butyl carbonium ion-catalyst complex

$$D^+:D^- + [C_4H_9]^+[AlCl_3X]^- \rightleftarrows C_4H_9D + D^+[AlCl_3X]^-$$
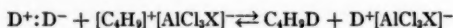
where X may be hydroxyl, chloride or hydride ion. It is evident that in this latter reaction the steady state concentration of carbonium ion is repressed. Since cracking reactions are known to be decreased to a larger extent than the isomerization by a reduction in the carbonium ion concentration, it is postulated that this reaction is responsible for the beneficial effect of hydrogen on the selectivity of the aluminum chloride catalyzed isomerization of pentanes and hexanes.

Tamaru & Boudart (48) examined the interaction of hydrogen with a germanium surface by measuring the direct adsorption, the desorption following germane decomposition, the hydrogen-deuterium exchange, and the decomposition of deuterogermane. The adsorption of hydrogen on a germanium film (prepared by the decomposition of germane on glass wool) was found to be activated, reversible, dissociative, and immobile, at least at low coverage, and was characterized by adsorption heats decreasing with coverage. The rate determining step of the decomposition of germane proved to be the desorption of hydrogen molecules from a monolayer of hydrogen atoms. The germanium surface which is reformed during decomposition did not exhibit a priori heterogeneity, and the decrease of adsorption heat with coverage was ascribed to induction. The observed isotopic rate effect for the for the decomposition of germane and for the desorption of hydrogen and deuterium indicates that the activation energy for the rate determining process does not correspond to some electronic barrier, but to the normal zero point energy difference of the hydrogen isotopes.

Burwell, Shim & Rowlinson (49) found an ingenious explanation for the discontinuities in the isotopic exchange pattern shown by certain cycloparaffins on reaction with deuterium at 60° to 80°C. The discontinuity appears markedly for cyclopentane and cyclohexane following the species of half deuteration, is very slight for cycloheptane, and disappears entirely for cyclooctane. Bicyclo(2,2,1)heptane exchanges only two hydrogen atoms. These results are consistent with the assumption that vicinally adsorbed alkane—a state equivalent to an adsorbed olefin—occurs only in the eclipsed conformation. Because of a certain rigidity of the rings, with cyclopentane eclipsed conformation can involve only *cis*-hydrogens, and therefore only half of the hydrogen atoms, located on one "side" of the molecule, can be exchanged. Cyclooctane is flexible enough to allow *trans*-hydrogens to be eclipsed, whereby the exchange can spread to both sides of the molecule. The cycloheptane molecule has some, but not sufficient, flexibility to eliminate the discontinuity completely. In bicyclo(2,2,1)heptane the four pairs of hydrogens on the ethylene bridges are rigidly held in eclipsed conformation, as are the two hydrogen atoms on the two bridgehead carbon atoms, but in

nearly staggered position relative to the adjacent methylene group. Thus, while the eclipsed vicinal adsorption necessary for the exchange is possible on the bridge, it cannot propagate to the next carbon atom. Hence only two hydrogen atoms are exchanged.

The mechanism proposed for the exchange involves successive dissociation to the half hydrogenated state and to the olefin followed by the reverse reactions, the rate of exchange being equal to the rate of adsorption. The high reactivity is ascribed to the low bond dissociation energy for the carbon-hydrogen bond. As the bond dissociation energy decreases in the order of primary, secondary, and tertiary carbon atoms, the rate of exchange increases. In the case of (+)3-methylhexane it was observed that nearly every molecule that underwent exchange was also racemized. Since vicinal diadsorption of the molecule will not cause racemization, it is suggested that the intermediate stage may be a monoadsorbed olefin.

Thomson & Walton (50) investigated the platinum-catalyzed hydrogen exchange between cyclohexene and tritiated and deuterated water. The exchange reaction involved all hydrogen atoms and was accompanied by double bond migration, the latter reaction being followed by the use of C^{14} labelled cyclohexene. If freshly distilled cyclohexene was used, in addition to these reactions disproportionation leading to the formation of benzene and cyclohexane also occurred. However, this reaction was poisoned by the hydroperoxide present in aged cyclohexene. The double bond migration was correlated with the exchange reaction in the 1,2-position and 3,4-position by the associative mechanism:
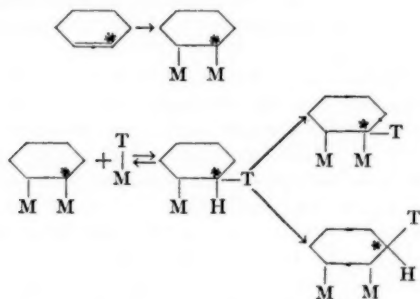
The catalytic deuteration of acetone on a great variety of evaporated metallic films was the subject of an extensive study by Kemball & Stoddart (51). The main product of the reaction was isopropanol by the successive additions of two deuterium atoms to the carbonyl groups of the adsorbed acetone molecules. Simultaneously, the methyl group was dissociatively adsorbed and underwent exchange. On palladium, gold, and silver the extent of the reduction was slow compared to the exchange. On nickel, iron, and tungsten the reduction was considerable, and with the two former metals

the accumulating isopropanol inhibited the exchange. The zero order dependence of deuteration and exchange on the acetone pressure and the initial distribution of deuteroacetones indicate strong adsorption of acetone by opening of the carbonyl double bond leading to a long contact time for the methyl group. The various possible exchange reactions, involving simple exchange on one or two methyl groups and multiple exchange on one or both methyl groups, occur to various extents on different metals. Of these, the simple exchange on one of the methyl groups by dissociative adsorption appears to be the most important. On platinum, palladium, and nickel multiple exchange on one methyl group is shown by the sudden decrease in the concentration of the acetone, d_4 as compared with the d_3 species. This observation indicates strong adsorption and long contact time, but the absence of rocking of the adsorbed acetone molecule. It is suggested that the rate determining step in the exchange is the desorption, and that the activation energies determined refer to the desorption. There appears to be some correlation between the d-character of the intermetallic bond and rate of desorption, lower d-character being connected with tight adsorption. The order of the activity of the metals studied for acetone exchange differs from the corresponding order for hydrocarbon exchange. The exchange for acetone is faster than for methyl groups in hydrocarbons. The difference is probably due to the difference in the nature of the adsorbed radical. For hydrocarbons the adsorption is weak and the slow step is the dissociative adsorption.

Addy & Bond (52) studied in detail the interaction of deuterium with cyclopropane, propene, propane, and propylchlorides on various catalysts in order to ascertain whether the previously found duality of distribution of deuterium in propane formed from cyclopropane in the presence of platinum was a unique observation.

When cyclopropane was reacted with deuterium over palladium, the reaction was proportional to the expression $[D_2]^x$ $[cyclo-C_3H_6]^y$, x and y having the values of -0.8 to 0, and 0.4 to 1, respectively, in the temperature range 50° to 200°C. The relative abundance of deuteropropanes formed was independent of the temperature or of the ratio of the reactants. The distribution of the deuteropropanes was highly unsymmetrical, the d_7 and d_3 species accounting for over 80 per cent of the total. These distributions can be ascribed to two random redistribution reactions involving a hydrogen pool of differing deuterium content, one of which, (a), leads to almost complete exchange of all hydrogen atoms, and the other, (b), involves the exchange of approximately half of the atoms.

In addition, there appears to be direct addition of deuterium to cyclopropane to a slight extent. The reaction between propane and deuterium at 100° to 200°C. on the same catalyst produced deuteropropanes of similar distributions, but the relative extent of the two random distributions was dependent on the temperature.

It is suggested that the two distributions arise in each case from reactions on different crystal faces of the metal, possibly on the *111* and the *100* planes.

The proposed mechanism involves the chemisorption of cyclopropane as the rate determining step. At low temperatures the surface will be saturated with physically adsorbed cyclopropane, and the rate will depend only on the concentration of pairs of sites unoccupied by hydrogen, hence the zero order with respect to cyclopropane and an order close to -1 with respect to hydrogen. At higher temperatures the surface is free of hydrogen and also of physically adsorbed cyclopropane, and the rate will be proportional to the hydrocarbon concentration. The next step is the rapid formation of propyl radicals which are then converted to either propane or adsorbed propylene, the latter reaction initiating the exchange. By addition of deuterium atoms, the adsorbed propylene molecules, in turn, can form either propyl or isopropyl radicals. The degree of exchange undergone by a radical depends on the ratio of the probabilities of its being converted to propylene or to propane. It is proposed that the most efficient exchange process occurs on the *111* plane since on this plane an adsorbed propyl radical can make a second point contact necessary for olefin formation in six directions, involving the most favorable interatomic distance of 2.74 A. This sequence of reactions leads to almost complete exchange of all of the hydrogen atoms; i.e., to reaction (a). Reaction (b) is thought to occur on the *100* planes.

When propane was reacted with deuterium on the same catalyst, a very similar isotopic distribution resulted, showing again propane-d_8 as the major product with two minor maxima for propane-d_2 and -d_4. In this case the initiating step for the exchange is the formation of an adsorbed isopropyl radical which then behaves in the subsequent steps in the same manner as the radicals formed from cyclopropane.

On the other hand, the propanes formed from propene by reaction with deuterium in the presence of palladium showed an entirely different isotopic distribution. The most abundant propane was, in almost all cases, the deuterium free species with a generally smooth decline in concentration with increasing deuterium content. This is attributed to the strong adsorption of propene on palladium in consequence of which the surface of the catalyst is covered mostly by adsorbed propylene and propyl radicals, their ratio being dependent on the D_2/C_3H_6 ratio. The close proximity of the adsorbed species makes inter-radical transfer reactions very readily possible, leading to the formation of deuterium-poor propanes.

The catalytic reduction of propylchloride and isopropylchloride to propane by deuterium in the presence of palladium catalyst—a rather slow reaction at 100°C.—once more gave an initial propane distribution that closely resembled the distribution found for cyclopropane, with the d_7 and d_8 species predominating. The slow step is presumed to be the formation of adsorbed propyl or isopropyl radicals by reaction with adsorbed deuterium atoms.

The reactions of cyclopropane and of propane with deuterium over rhodium and iridium catalysts gave a picture similar to that obtained with palladium.

Diffusion and mass transfer.—A number of papers have dealt with the too often neglected effects of diffusion and mass transfer on the kinetics of catalytic reactions.

Freund & Hulburt (53) studied the kinetics of the hydrogenation of acetone (to isopropanol), acetophenone (to 1-phenylethanol) and styrene (to ethylbenzene) catalyzed by Raney nickel. The experimentally observed order of these reactions, m, with respect to hydrogen was $m = 1/2, 1/2$ and 1, respectively, while the experimental activation energies, E_e were 8, 13, and 15 kg. cal./mole, respectively. Because of the relatively low value of the activation energies it was suspected that diffusion in the pores may play an important role. Using a treatment similar to that developed by Wheeler (54), the fraction of the pore surface available was calculated and found to be 10^{-1} to 10^{-8}, indicating control by diffusion. For such a case the intrinsic (true reaction order, n,) for the nonporous catalyst is $n = 2m - 1$, and the intrinsic energy of activation, $E_i = 2E_e + (n+1)H + E_d$ where H is the heat of solution of hydrogen and E_d is the energy of activation for diffusion in the liquid. These relations then give $n = 0$, 0 and 1, and $E = 13 \pm 2$, 23 ± 2, and 27 ± 2, kg.cal./mole respectively, for the studied reactions.

Weisz (55) discussed the measurement of the diffusivity of porous catalyst particles and the significance of this quantity for heterogeneous reactions.

Andrussow (56) developed formulae for the kinetics of ammonia synthesis along a catalyst bed using a previously suggested diffusion equation and introducing the concept of "critical" concentration at which the velocity on the catalyst is equal to the rate of transport.

Noller & Hässler (57) studied diffusion effects in the decomposition of diazoesters in aqueous solutions catalyzed by sulfonated polystyrene ion exchange resins.

Price & Schiewetz (58) studied the catalytic hydrogenation of cyclohexene in the liquid phase using a batch type reactor and flowing hydrogen. However, under the reaction conditions the mass transfer of hydrogen to the catalyst-liquid phase interface was found to be the dominating effect and therefore it was not possible to achieve a true rate controlling reaction. The authors point out the necessity of evaluating the hydrodynamic factors in this type of system in order to obtain fundamental chemical information.

The mixing of fluidized cracking catalyst in a commercial reactor [Singer, Todd & Guinn (59)] and the loss of fresh catalyst [Todd & Wilson (60)] was followed by employing radioactive catalysts.

Miscellaneous organic reactions.—During the year 1957 the studies concerned with catalytic reaction mechanisms centered mainly around hydrocarbons and dealt with hydrogenation, polymerization, alkylation, cracking, aromatization, and isomerization.

From magnetization-volume adsorption isotherms Selwood (61) obtained some interesting information on the chemisorption of hydrogen, ethylene, and benzene, and on the catalytic hydrogenation on nickel. This

method is based on the observation that chemisorbed gases change the density of the d-band electrons and thereby the specific magnetization of catalytically active solids. Transfer of electrons to the chemisorbed gas to the solid will decrease the magnetization, while the opposite effect will occur on the transfer of an electron to the adsorbed gas.

If hydrogen is admitted to a supported nickel catalyst, the specific magnetization, σ_0, decreases linearly with the amount of chemisorbed hydrogen. According to Broeder et al. (62), one should be able to calculate the loss of magnetization, $\Delta\sigma$, from the formula $\Delta\sigma/\sigma_0 = \pm n/0.6N$, where n and N are the nickel atoms on the surface and in the total solid, respectively, and 0.6 is the number of unpaired electron spins per nickel atom. A comparison of the calculated and observed values for the loss of magnetization on adsorption of hydrogen for various nickel catalysts shows wide discrepancy, in some cases the calculated values, in others the experimental values, being higher. One explanation for this difficulty would be the assumption of different bond types for nickel-hydrogen in various samples. The other explanation, favored by Selwood, is connected with the failure of very small particles of nickel to be ferromagnetic at room temperature. Since such particles will chemisorb hydrogen without contributing to the magnetization, the experimental magnetization-volume isotherms do not give the correct correlation between loss of magnetization and hydrogen taken up by the particles actually under magnetic observation. Another effect which will give higher loss of magnetization than calculated is the lowering of the Curie point by the pairing of all electrons in the surface atoms.

If, nevertheless, it is assumed that each chemisorbed hydrogen atom contributes one electron to the nickel particle to which it is attached, the following picture may be made of the surface reactions involving the system nickel-ethylene-hydrogen-ethane.

Since the initial slope of the magnetization isotherm for ethylene is somewhat larger than that for hydrogen, it appears that the nickel receives on the average a little more than two electrons per molecule of ethylene chemisorbed. This would mean that the major portion of the ethylene is held by two point attachment while a smaller fraction dissociates into hydrogen and acetylenic radicals, requiring four or more sites per molecule. From the ratio of the volumes of chemisorbed hydrogen and of ethylene it is concluded that there are approximately three times as many sites available for hydrogen adsorption as for ethylene adsorption.

If hydrogen is chemisorbed on nickel already saturated with ethylene, the slope of the magnetization isotherms is about 2.4 times less steep than that for the corresponding hydrogen isotherm on bare nickel, indicating that the number of electrons transferred per hydrogen atom chemisorbed is 2.4 times less on an ethylene saturated surface. These observations are compatible with a situation in which, out of four chemisorbed hydrogen molecules, two are adsorbed on sites accessible to hydrogen only, one reacts with chemisorbed ethylene to form ethane, and the fourth takes the place of the ethylene

molecule. Accordingly, in this case, the net electron transfer to the nickel is only 1/2 per atom of hydrogen.

Since the initial magnetization slope for ethane on bare nickel is twice that for ethylene and over four times that for hydrogen, the chemisorption of ethane requires at least four sites per molecule, indicating dissociative adsorption, the total amount of ethane chemisorbed being about half of the volume of ethylene which can be chemisorbed. No change in the magnetization was observed when ethane was admitted to nickel already covered with chemisorbed hydrogen.

The results with ethylene are apparently in contradiction with experimental data concerning the inhibition of the hydrogen-deuterium exchange reaction by chemisorbed ethylene and the fragmentation of ethylene on nickel indicated by the infrared studies of Pliskin & Eischens (63). It appears that on the supported nickel catalyst used by Selwood, fragmentation of ethylene, which is also responsible for the inhibition of the hydrogen-deuterium exchange reaction, occurs only at elevated temperature, but not at room temperature, at which the magnetic measurements were carried out. On the other hand, on nickel wire or nickel film fragmentation of ethylene takes place more readily.

For the system nickel-benzene-cyclohexane analogous studies were made covering temperatures up to 150°C. Both benzene and cyclohexane are chemisorbed on nickel-silica at room temperature, as shown by the drop of magnetization, but the quantitative evaluation of the data is not possible because of the concurrently occurring van der Waals adsorption. At 150°C. the van der Waals adsorption is not much in evidence and the loss of magnetization by the chemisorption of benzene or of cyclohexane is three to six times the effect caused by an equal number of hydrogen molecules. On the assumption that each chemisorbed hydrogen molecule forms two nickel-hydrogen bonds and that the magnetic effects of the nickel-hydrogen and nickel-carbon bonds are equivalent, these observations are interpreted by postulating a minimum six bond attachment for benzene, and a minimum eight bond attachment for cyclohexane. In the former case this type of chemisorption would correspond to benzene lying flat on the surface, while in the case of cyclohexane, it would involve dissociative adsorption comprising four carbon-nickel and four hydrogen-nickel bonds.

Addition of hydrogen to a surface already covered with benzene yields almost the same initial slope for the magnetization curve as on bare nickel, indicating preferential chemisorption of hydrogen rather than hydrogenation. On continuing the addition of hydrogen, the magnetization curve gradually flattens. This is taken as indication that the nickel-carbon bonds are being replaced by nickel-hydrogen bonds. The total volume of hydrogen taken up is equal to the amount required to cover the surface and to hydrogenate the benzene which was originally chemisorbed.

No hydrogenation is observed if hydrogen is added at −77°C. to the nickel covered with benzene, nor is any hydrogenation or chemisorption of

benzene in evidence at 25°C. on nickel partially covered by hydrogen. Apparently the initially chemisorbed hydrogen is too tightly bound to allow reaction. If now more hydrogen is added, gradually the surface is completely covered and the nickel-hydrogen bond is weakened sufficiently for the chemisorbed hydrogen to undergo reaction with physically adsorbed benzene. Actually this behavior was demonstrated directly by continuously recording magnetization versus time during the removal of hydrogen from the nickel by benzene, resulting in the final increase of magnetization.

Devereux *et al.* (64) investigated the catalytic hydrogenation of N,N-dimethyl-*m*- and -*p*-toluidine, pyridine, pyrrole, quinoline, N,N-dimethylphenethylamine, and benzylamine on Adams' platinum oxide catalyst in order to elucidate the effect of self poisoning of the catalyst by these nitrogen compounds. It was found that "unshielded" nitrogen is nontoxic if adjacent to an aromatic ring, but toxic if adjacent to a saturated system. This lessened availability of the lone electron pair of the nitrogen atom adjacent to an aromatic ring for coordinate bond formation with the platinum parallels the base strength of the amine. The weak aromatic bases are nontoxic while the stronger alicyclic bases are toxic. In the presence of an acid, such as hydrochloric acid, the stronger base formed during hydrogenation is converted into a salt (by replacing the weaker base) and can thus be rendered nontoxic.

Maxted & Biggs (65) reported on the poisoning effect of dry ammonia on the platinum catalyzed hydrogenation of olefins. The results were interpreted in the light of the previously suggested mechanism of nitrogen and sulfur detoxification. A parallelism was shown to exist between poisoning of enzymes and of catalysts by nitrogen compounds.

A unique catalytic method for the synthesis of pure benzene-D_6 was found by Shapiro & Weiss (66). Houdry M-46 catalyst is first treated with diborane to remove traces of water, then deuteroacetylene, C_2D_2, is circulated over the catalyst. Finally the catalyst is heated to 150°C. to recover adsorbed deuterobenzene in 50 per cent yield. Interestingly, no deuterium exchange takes place with the catalyst, while benzene with statistical distribution of hydrogen and deuterium is formed from a mixture of acetylene and deuteroacetylene.

Kawaguchi (67) found that the catalytic polymerization of propane on a nickel oxide-kieselgühr catalyst followed the Zeldowitch equation. From the relation of the initial rate of reaction and the initial adsorption at various pressures it was concluded that the reactant molecules participate in the reaction via the van der Waals layer, either their chemisorption or their addition to the growing chemisorbed polymer being the rate determining step. The Zeldowitch equation obtains because the rate constant decreases as monomer units in surface complex increase.

Natta & co-workers (68) studied the polymerization of propene dissolved in heptane in the presence of a catalyst prepared from macrocrystalline titanium trichloride and triethyl aluminum. The rate of polymerization in-

creased gradually and reached a steady value after one to five hours. This rate was proportional to the amount of solid catalyst and to the propene pressure, and was independent within wide limits of the triethyl aluminum concentration. The increasing rate of reaction was attributed to the mechanical disintegration of the solid titanium trichloride by the action of triethyl aluminum, since titanium trichloride has a lattice consisting of layers of titanium and chloride ions which can be readily cleaved. This concept was confirmed by the elimination of the induction period after mechanical grinding. The active catalyst is thought to be a surface complex formed by the solid titanium compound and the aluminum alkyl. It is suggested that the positive aluminum atom and a negative —CH_2— are involved in the growth of the polymer. In the propylation step polarized olefin molecules are inserted between the aluminum and the —CH_2— group.

The side chain alkylation of aromatic hydrocarbons and related reactions in the presence of organo-sodium compounds and various metal hydrides were studied by Voltz (69). With phenyl sodium or sodium-anthracene as the catalyst, for example, toluene was readily ethylated at 200°C., while alkali metal hydrides were active only at 300°C. Alkaline earth metal hydrides were inactive.

In order to test more completely the current stepwise mechanism suggested for the Fischer-Tropsch mechanism [Storch *et al.* (70), and Kummer & Emmett (71)], Kokes, Hall & Emmett (72) investigated the incorporation of radioactive ethanol in the synthesis products on a variety of catalysts at pressures up to 21 atm. A nitrided doubly promoted iron catalyst was included among the catalysts studied since this catalyst gives unusually high yields of alcohols and thus allows the comparison of the distribution of radioactivity in the alcohols and in the hydrocarbons present in the synthesis products.

The incorporation was the highest for a reduced singly promoted iron catalyst and decreased in the sequence: reduced doubly promoted iron, nitrided doubly promoted iron, reduced cobalt. The incorporation also decreased with increasing synthesis pressure and decreasing ethanol content in the feed. At incorporations lower than 20 per cent the plot of the molar radioactivity of the hydrocarbons versus carbon number showed a maximum in the C_3–C_4 region, and usually a minimum at C_5. In general, the variation of the radioactivity with carbon number increased as the incorporation decreased. In the case of the nitrided catalyst, the average molar radioactivity of the alcohols formed was the same as for the hydrocarbons but the dependence of the radioactivity on the carbon number was different, showing a minimum at C_4. With the cobalt catalyst the maximum radioactivity was found for the C_2 fraction.

From these observations it is concluded that, in agreement with previous suggestions, an adsorption complex formed from the ethanol is the principal intermediate involved in the initiation of the formation of a hydrocarbon

chain. However, this intermediate is not built into the chain, since such a step would show increasing molar radioactivity with carbon number. The dependence of the incorporation on pressure, alcohol concentration, and catalyst composition can be interpreted on the basis of the stepwise growth of the hydrocarbon chain and a Langmuir type adsorption isotherm for alcohol for which the adsorption is medium strong. The ethanolic complex differs from the initiating C_1 complex formed from carbon monoxide and hydrogen, and the two complexes compete as initiators. While these alcoholic complexes are mainly responsible for chain initiation, other species are probably also involved, one of which may be related to ethylene formed by dehydration of ethanol. This latter complex may be directly hydrogenated and, in the case of the cobalt catalyst, give rise to the maximum activity for C_2. The similarity of the radioactivity of the hydrocarbons and of the alcohols formed on the nitrided catalyst is taken as an indication that both types of products are initiated by the same complex.

The same authors (73) also extended the earlier studies on the participation of methanol in the Fischer-Tropsch synthesis to higher pressures in order to obtain some information on the mechanism under conditions similar to those of the commercial synthesis. In agreement with earlier results obtained at atmospheric pressure (71) it was found that at 7.5 atm. the radioactivity of the hydrocarbons formed on reduced iron catalyst at 230°C. in the presence of 1 per cent radioactive methanol increased with increasing number of carbon atoms, indicating that the methanol forms a complex on the catalyst that is capable of initiating hydrocarbon synthesis and probably also of entering the chain-building step. The latter conclusion was deduced from the fact that the radioactivity of the hydrocarbons formed was higher than that calculated on the basis of the radioactivity of the carbon monoxide resulting by the slight decomposition of the methanol. An appreciable amount of carbon dioxide was also found to form directly from methanol.

When radioactive carbon dioxide was admixed to 50:50 hydrogen-carbon monoxide mixture at atmospheric pressure, very little carbon monoxide was converted to either carbon dioxide or hydrocarbons at 240°C. on the iron catalyst. It appears that the water gas shift reaction is rather slow under these conditions. Formaldehyde decomposed almost completely to carbon monoxide and hydrogen, but also formed some carbon dioxide directly. In this case the radioactivity of the carbon monoxide in the gas stream was sufficient to account for the activity versus carbon number plot of the hydrocarbons formed. The slope of this plot shows that a few hydrocarbon chains are initiated by a complex formed from the formaldehyde and that this complex is different from the initiating complex derived from carbon monoxide and hydrogen in the absence of formaldehyde.

Darby & Kemball (74) used vapor phase chromatography to study the decomposition of methanol on a cobalt Fischer-Tropsch catalyst in order to ascertain the relation of decomposition to synthesis. At 160° to 210°C. the

decomposition yielded carbon monoxide and hydrogen only, the amount of hydrocarbons and of other synthesis products being less than 1 per cent. It is suggested that the reaction mechanism involves the intermediate:

$$
\begin{array}{cccc}
H & CH_2{-}O & H \\
\vdots & \vdots & \vdots & \vdots \\
M & M & M & M
\end{array}
$$
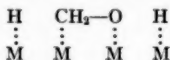
The complex [—CH$_2$—O—] then decomposes to carbon monoxide and hydrogen. Accordingly, methanol is incorporated into the hydrocarbons only indirectly via carbon monoxide. The experimental results are compatible with the possibility of the complex [—CH$_2$—O—] isomerizing into the complex [>CH—OH], suggested by Storch *et al.* (70) as the intermediate in the Fischer-Tropsch reaction, provided such isomerization is slow.

By potential measurements on the platinum metals during the decomposition of formic acid to hydrogen and carbon dioxide, Schwabe (75) found support for the concept that the metal catalyst is an electron acceptor. The shift of the potential by aqueous formic acid to negative values was ascribed to the shifting of electrons from chemisorbed formic acid to the conductivity bands of the metal. From the pH dependence of the catalysis it is concluded that molecules, and not ions, of formic acid are involved in the reaction.

Plank *et al.* (76) examined the characteristics of silica-alumina, silica-magnesia and fluoride treated silica-alumina for cracking methylcyclohexane and *n*-decane. The products were carefully analyzed and the data correlated to indicate differences among the catalysts. The results were explained on the basis of the important over-all reactions of carbon chain splitting, hydrogen transfer, and polymerization.

Maatman, Lago & Prater (77) studied the effects of inhibitors on the cracking of cumene on silica-alumina. The inhibitors, various hydrocarbons, oxygen, sulfur and nitrogen compounds, compete with cumene for the cracking sites on the catalyst. The equilibrium constant for the adsorption of the inhibitors can be calculated from an expression derived for the rate of cracking.

The most important reaction occurring in naphtha-reforming by platinum type dual function catalysts is the formation of aromatic hydrocarbons. While the conversion of cyclohexanes to aromatics is readily accomplished by simple dehydrogenation, the reforming of cyclopentanes requires first the isomerization of the five membered naphthenes to six membered structures. It has been suggested by Mills *et al.* (78) that this type of isomerization involves the dehydrogenation of the saturated hydrocarbons to olefins and that the olefins thus formed are then isomerized under the influence of the acidic function of the catalyst. It is readily seen that in such a reaction sequence the over-all reaction rate will be controlled by the slower of the two reactions, dehydrogenation and isomerization.

Weisz & Prater (79) sought to correlate the individually measured dehydrogenation function (measured by cyclohexane dehydrogenation) and

acidic function (measured by cumene dealkylation) of a number of dual-function reforming catalysts with their over-all reforming activity. With a great variety of platinum catalysts in various stages of activity the results showed the following: The reforming activity decreased with the dehydrogenation function if the latter was below a certain critical value. Above this critical value the reforming activity was independent of the dehydrogenation function but was controlled by the acidic function. These conclusions are consistent with the mechanism proposed by Mills *et al.* (78).

Weisz & Swegler (80) have also provided a direct experimental proof for the mechanism suggested by Mills *et al.* (78) for the isomerization of saturated hydrocarbons on dual function catalysts. These authors have shown that the isomerization of *n*-hexane to isohexanes at 373° and 448°C. was four to twenty times faster in the presence of a mixture of a platinum catalyst on inert support and a silica-alumina cracking catalyst than in the presence of either of the two catalysts alone. This observation is explained by a three step reaction involving dehydrogenation on the platinum catalyst, isomerization of the resulting hexene on an adjacent silica-alumina particle, and, finally, hydrogenation of the isohexene molecules on the platinum. In the case of the isomerization of *n*-heptane at a pressure of 25 atm. and a partial pressure of 20 atm. of hydrogen, it was shown that rate of isomerization depended on the particle size and that the rate with mixed catalyst of 10 to 100 μ particles was almost as fast as with actual dual-function catalysts.

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PHYSICAL ORGANIC CHEMISTRY[1,2]

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A reasonable definition of the domain of *Physical Organic Chemistry* was given seventeen years ago by L. P. Hammett, in his inspiring book by this title, as one concerned with investigations of organic chemistry by quantitative and mathematical methods. The chief directions of the field were given as (*a*) mechanisms of reactions, and (*b*) the effects of structure and environment on reaction rates and equilibria.

The amount of significant research reported during the current year which falls within these confines has been so enormous that it early became apparent to us that to cover such an area would scarcely enable us to prepare a running list of titles. Consequently we have chosen for detailed review only four admittedly narrow topics within the realm. In so doing it is our hope that our modest efforts at review will provide something of use to those interested in our topics. No claims are made as to the relative merits of topics considered or not considered, and we trust that it will be possible for subsequent reviews under this title to pick up many of the important contributions which we have neglected. Inasmuch as the previous review of this area was devoted to reaction mechanisms, we have devoted much of our attention to the second of the chief directions of the field.

SIGMA VALUES AND THE EFFECTS OF STRUCTURE ON REACTIVITY

Introduction

The approximate empirical correlation and prediction of the polar effects of substituent groups on reaction rates and equilibria by means of sigma values has been the subject of continuing interest for a number of years. The procedures and applications of the method have been extended in recent years so that a review of the present status of this approach to the understanding of the effects of molecular structure on reactivity is appropriate.

The basic tool of the sigma value approach is the quantitative linear correlation of the effects of substituent groups on the logarithm of rate constants, equilibrium constants or quantities derived from appropriate differences between these. The correlations are made between corresponding substituent effects in various reaction series (a series of reactions involving a common functional group, reagent, mechanism, and set of experimental

conditions) with a particular reaction series serving to define the sigma values.

The interest in sigma value correlations follows along several distinct lines. First, to the extent and to the precision with which sigma values find general application (sigma correlations are by no means exact relationships), the theoretical interpretation of polar effects in terms of field, polarization, electron-displacements through bonds, resonance, and solvation phenomena, instead of being a separate problem for each type of reaction rate or equilibrium, becomes only a problem of interpretation of sigma values (1a).

Second, the sign and magnitude of the coefficient of correlation (the rho value) provides a constant characteristic of the nature of the change occurring at the reaction center which has found important application in mechanism studies (1a, 2a).

Third, the method provides a simple and readily applicable procedure for storage of data and the empirical prediction of polar effects (1a). If the observed effects of a wide variety of substituents correlate with sigma values, effects other than polar may be assumed negligible (1a, 2b). For substituents introduced directly at the reaction center such a demonstration is indicative of a characteristic structural change at the reaction center (2a).

Fourth, if effects other than polar contribute to those observed, the empirically predicted polar effect may enable the approximate evaluation of these other variables (2c, 3a). That is, the investigator is presumably placed in a favorable position for carrying out unambiguous and near-quantitative studies of other effects of molecular structure on reactivity.

Developments of the current year have been concerned particularly with this fourth application of sigma values. The theoretical model assumed (2d, 3b) in this connection is that frequently the effect of structure on the free energy change (activation or reaction) may be treated to give a useful approximation as the sum of independent polar, resonance, and steric effects (for definitions of these terms as employed in this review, see references 2d and 3b). Applications which have been made include: the evaluation of resonance effects, hyperconjugative and conjugative, in both the aromatic and aliphatic series; (b) determination of the extent of steric inhibition of resonance; (c) determination of steric inhibition of solvation; (d) evaluation and correlation of intramolecular steric effects; and (e) evaluation of driving forces involved in anchimeric assistance (neighboring group participation).

The Hammett Equation

The Hammett linear free energy relationship, $\log (k/k_0) = \sigma\rho$, was derived from the observation that plots of the logarithm of the rate or equilibrium constants for the reactions of a series of m- and p-substituted derivatives of benzene vs. the logarithm of the ionization constants for the correspondingly substituted benzoic acids in water at 25°C. are very frequently linear (1a). Introducing the definitions, $\log (K/K_0) \equiv \sigma$ and $\rho \equiv 1.000$ for the ionization benzoic acids in water at 25°C. (the subscript zero refers to the

unsubstituted benzoic acid), Hammett obtained his well-known relationship.

The σ value has been associated with the effect of the substituent on the charge density of the carbon atom which bears the side-chain reaction center. Both classical electrostatic (inductive) and resonance interactions of the substituent with the benzene ring are reflected in σ values (1a, 4). A positive value of σ denotes net electron-withdrawal relative to the hydrogen atom, and a negative value, the contrary. The quantity ρ (a property of the process involved) measures the susceptibility to changes in electron density. A positive value of ρ indicates that the process in question is accompanied by a decreased electron-demand at the reaction center, and vice versa.

It is now quite clear that resonance effects resulting from direct conjugation between substituent and reaction center are one of the principle causes of failure of the Hammett equation, or, in the more fortunate cases, of the utility of "dual" substituent constants (1a, 2a, 3c, 4, 38).

Jaffé (4) has reviewed the Hammett relationship and gives a valuable discussion and summary of σ and ρ values. McDaniel & Brown (5) have more recently completed a comprehensive review of the data on the ionization of substituted benzoic acids. These authors recommend strict adherence to Hammett's definition of sigma values based upon these ionization data, rather than upon mean values derived from the fit of all available reactivities to the Hammett equation. The latter procedure was employed by Jaffé for substituents for which σ values were not assigned by Hammett. A number of values virtually equivalent to those of McDaniel & Brown are listed in Table I.

A summary of work (necessarily incomplete) from the literature of the current year which pertains to the Hammett equation is collected in the bibliography. References 6 to 30 deal with correlations of reaction rates or equilbria, references 31 to 35 with correlations of physical properties, and reference 36 deals with theoretical aspects of the Hammett equation. The use of "dual" substituent constants in the correlation of electrophilic and nucleophilic substitution in the benzene ring has been extended (37). A novel application of the Hammett equation has been made in the study of the mechanism of the acid-catalyzed Schmidt rearrangement of aryl azides (6). Both the rates of nitrogen evolution and the product ratios of m- or p-substituted benzaldehyde to benzaldehyde from the Schmidt reaction of m- and p-substituted benzhydrols, $(X-C_6H_4)(C_6H_5)CHOH$, are shown to follow the Hammett equation. The relationship between the two values of rho obtained is shown to exclude a one-stage mechanism in which nitrogen evolution and the migration of the aryl group are synchronous.

THE INDUCTIVE CONSTANTS OF BRANCH AND CALVIN

A comprehensive qualitative theory of inductive effects has been developed over the years particularly under the impetus of the English school (39a). The theory was first applied in quantitative form to acid ionization equilibria by Branch & Calvin (3b). Using both mineral and carboxylic

acids derived from H_2O, it was shown that numerous ionization constants in water at 25°C. (covering the range $K_a = 10^{-16}$ to 10^{-1}) can be calculated with an accuracy on the order of a power of ten by assigning an empirical inductive constant to each atom and to each formal charge on an atom.

σ^* VALUES

A procedure somewhat different in form, and based upon reaction rates, was employed recently by Taft for quantitatively evaluating inductive effects. An original suggestion by Ingold (40) was extended (41), employing a substituent constant approach analogous to that of Hammett. A polar substituent constant, σ^*, for a group R relative to the CH_3 group was defined by the equation: $\sigma^* \equiv (1/2.48) [\log (k/k_0)_B - \log (k/k_0)_A]$.

The symbol k refers to the rate constant for the normal hydrolysis of an ethyl ester of the formula $RCO_2C_2H_5$; k_0 is the rate constant for ethyl acetate. The subscripts B and A refer to the alkaline saponification and the acid-catalyzed hydrolysis reactions, respectively, under otherwise identical conditions of solvent and temperature. The factor $1/2.48$ is an arbitrary constant. The reasoning associated with this procedure has been discussed (40, 42, 2e).

Values for σ^* are in satisfactory accord with the qualitative scale of polarities of the English school. Several quantitative relationships to structure expected of polar effects, such as approximate additivity, are exhibited (2a). A number of qualitative relationships between σ^* values and concepts of bonding and electronegativity have been discussed (42). For substituents of the general formula XCH_2, σ^* values bear a close quantitative correspondence to the inductive constants for X of Branch & Calvin [see reference (43)].

The σ^* values have been found to correlate in a quantitative fashion the effects of structure on a variety of reaction rates and equilibria of the general type $R—Y + Z \rightleftarrows P$ (R, substituent, Y, functional group, Z, reagent, and P, the reaction transition state or the reaction products) given relative to that for the $CH_3—Y$ molecule (41). The correlation equation is log $(k/k_0) = \sigma^*\rho^*$. ρ^* is a reaction susceptibility constant analogous to the ρ of the Hammett equation. A compilation of σ^* and ρ^* values is available (2a to g). Several correlations reported recently are collected in the bibliography (44 to 47) and others are discussed in later sections.

The implied criterion for correlation by this equation is that inductive effects govern reactivities within the reaction series. It is maintained that the equation demonstrates a general applicability of σ^* values to the correlation and prediction of inductive effects (2a). The equation has also been taken as an indication that an approximately quantitative scale of polarities is not appreciably altered by the absolute electron density of the atom to which the substituent is bonded (42).

The σ_I scale of inductive effects.—In accord with the last conclusion above, evidence has been found that the order of inductive effects obtained from

the aliphatic series applies to the inductive contributions to reactivities in the aromatic series (2f). An inductive substituent constant for the group X has been defined (2f, 48) as $\sigma_I = (0.45)\ \sigma^*_{XCH_2}$ (this definition places the σ_I scale relative to the hydrogen atom instead of the CH_3 group). It is proposed that to a useful quantitative approximation the σ_I value is equal to the inductive contribution to the Hammett σ value for either m- or -p-substituents (charged substituents have been excluded). The evidence on which this proposal was based is considered in the section on Ionization of benzoic acids.

The "normalization" factor, 0.45, used in obtaining σ_I values is apparently justified on the basis of the results obtained with its use. However, this value was obtained by considering the important studies of Roberts & Moreland (49) on the reactivities (σ' values) of 4-substituted bicyclo-[2.2.2]-octane-1 derivatives (2f).

RESONANCE EFFECTS IN THE AROMATIC SERIES

Ionization of benzoic acids.—The contribution to the logarithm of the ionization constant of a p-substituted benzoic acid (in water at 25°C.) which results from the existence of π-bond resonance interaction between the substituent and the benzene π-orbitals, is obtained (2f, 48, 48a) from the quantity, $\log (K^pK_0) - \sigma_I = \sigma_p - \sigma_I$. The resonance effect so determined has been given the symbol, σ_R, i.e, $\sigma_R \equiv \sigma_p - \sigma_I$.

A partial summary of recently obtained σ_R values is given in Table I. These σ_R values were obtained from σ values based only upon the ionization of benzoic acids (5) and the rate of saponification of benzoate esters. Uncertainties in the σ and σ_I values of Table I are generally on the order of ± 0.03 so that the general order of uncertainty in σ_R values is ± 0.04.

Values of σ_R are negative for groups which are *ortho-para* directing in electrophilic aromatic substitution and positive for the *meta*-directing groups. Satisfactory agreement exists between the values of σ_R and Ingold's qualitative scale of mesomeric effects (39b). In spite of widely varying values of σ_p, σ_m, and σ_I, the relationship $\sigma_m = \sigma_I + \frac{1}{3}\sigma_R$ is followed by all noncharged substituents within the uncertainties of the sigma values. These relationships, which provided the basic line of evidence (2f) for the validity of the separation of σ into σ_I and σ_R, were first noted (49) in terms of $\sigma - \sigma'$ values for the OH, Br, and CN, and $CO_2C_2H_5$ substituents. Other relationships of σ_R values to structure have been discussed (2f).

A resonance contribution to the σ value for a *meta*-substituent equal to approximately one-third of that for the corresponding *para*-substituent (the relationship $\sigma_m = \sigma_I + \frac{1}{3}\sigma_R$ is illustrated by $\sigma_p - \sigma_I$ and $\sigma_m - \sigma_I$ values given in Table I) is considered (2f, 49, 50) to result from indirect inductive transmittal of the effects of resonance interaction of the *meta*-substituent with the position *ortho* (and *para*) to the side-chain reaction center (39c). Confirming evidence is given in the section on nuclear magnetic shielding in fluorobenzenes.

In the subsequent discussion, substituents which are electron-withdraw-

TABLE I

Summary of Sigma Values

Substituent	σ_p	σ_m	σ_I	$\sigma_R \equiv \sigma_p - \sigma_I$	$\sigma_m - \sigma_I$
NH_2	−0.66	−0.15	+0.10	−0.76	−0.25
OH	−0.35	+0.08	+0.25	−0.60	−0.17
OCH_3	−0.26	+0.08	+0.25	−0.51	−0.17
F	+0.08	+0.35	+0.52	−0.44	−0.17
SCH_3	−0.05	+0.15	+0.25	−0.30	−0.10
Cl	+0.23	+0.37	+0.47	−0.24	−0.10
$NHCOCH_3$	+0.06	+0.21	+0.28	−0.22	−0.07
Br	+0.23	+0.39	+0.45	−0.22	−0.06
$(CH_3)_3C$	−0.16	−0.11	−0.07	−0.09	−0.04
I	+0.28	+0.35	+0.39	−0.11	−0.04
CH_3	−0.16	−0.07	−0.05	−0.11	−0.02
C_6H_5	−0.01	+0.06	+0.10	−0.11(+.09)	−0.04
$OCOCH_3$	+0.30	+0.37	+0.39	−0.09	−0.02
H	0.00	0.00	0.00	0.00	0.00
$N(CH_3)_3^+$	+0.86	+1.00	+0.86	0.00	+0.14
$SOCH_3$	+0.56	+0.53	+0.52	+0.04(+.20)	+0.01
CF_3	+0.50	+0.42	+0.41	+0.09	+0.01
$(CH_3)_3Si$	−0.03	−0.08	−0.12	+0.09	+0.04
CN	+0.68	+0.62	+0.58	+0.10(+.41)	+0.04
$C_2H_5O_2C$	+0.43	+0.36	+0.32	+0.11(+.36)	+0.04
CH_3SO_2	+0.71	+0.65	+0.59	+0.12(+.46)	+0.06
CH_3CO	+0.43	+0.35	+0.28	+0.15(+.60)	+0.07
NO_2	+0.79	+0.71	+0.63	+0.16(+.64)	+0.08

ing by resonance interaction are designated as +R substituents and electron-releasing ones as −R substituents.

Ionization of phenols.—Enhanced effective σ values for +R groups are required to correlate the effects of these substituents on the ionization of phenols (1a, b, c). Values of the enhanced constants [now given (48) the symbol, σ^-] based upon reactivities of derivatives of aniline and phenol have been given (4). The enhanced acid-strengthening effect is attributed to a conjugation between the +R substituent and reaction center which is greater in the phenoxide ion than in the phenol molecule (3c). The enhanced resonance effect has been represented (48) by the resonance substituent constant, σ_R^-, obtained from σ^- values by the defining relationship: $\sigma_R^- \equiv \sigma^- - \sigma_I$. Values of σ_R^- are listed in the parenthesis in Table I. It is worthy of note that σ_R^- values are approximately four times greater than corresponding σ_R values.

This latter relationship cannot be universal, however, as illustrated by the interesting results obtained (19) with the β-nitrovinyl group. Values of σ_m and σ_p for this group have been determined for the ionization of benzoic

acids and phenols, from which the following values are obtained: $\sigma_I = +0.38$, $\sigma_R = -0.12$, and $\sigma_R^- = +0.50$. The negative value of σ_R is in accord with the fact that this group is *ortho-para* directing in electrophilic aromatic substitution (51). On the other hand, the highly positive σ_R^- value bears striking testimony to the strong dependence which the functional group may exert on the R effect of a substituent.

A valuable investigation of the effects of $-R$ groups on the ionization of phenols has been made (52). These substituents, particularly from the *para*-position, deviate widely from a reasonably precise line followed by many (but not all) *meta*-substituents in a plot of log K_a for ionization of phenols vs. log K_a for ionization of benzoic acids. Using essentially the slope of the line for *meta*-substituents as the ρ value for the ionization of phenols, effective σ values have been calculated. Based upon the quantity, $\sigma_p - \sigma_m$, it is shown that the resonance effects of $-R$ groups in the ionization of phenols are relatively small and not related (the order is inverted for NH_2 and OCH_3, for example) to those of the corresponding groups in the ionization of benzoic acids ($2/3 \, \sigma_R$ values). The authors attribute this result to conjugation effects (analogous to those of $+R$ substituents in the ionization of phenols) of the $-R$ substituents in the ionization of benzoic acids. However, the result appears to be better explained as arising from a "leveling effect" on the substituent electron-release by the powerfully electron-releasing phenolate ion (3c).

Nuclear magnetic shielding in fluorobenzenes.—An extensive investigation (53, 53a) of the effects of substituents on the nuclear magnetic resonance lines of fluorobenzenes revealed that the δ^F values for *para*-substituents are apparently more dependent upon resonance interactions than corresponding σ_p values. A relatively precise correlation of these shielding effects has been made (48), according to the following equations, which involve different rho values (susceptibility factors) for inductive and resonance contributions:

$$\delta_m^F = (0.58)\sigma_I; \qquad \delta_m^F = (0.58)\sigma_I + (1.88)\sigma_R$$

The correlation for *para*-substituents is limited to $-R$ substituents. For the $+R$ substituents a resonance parameter having a value intermediate between σ_R^- and σ_R is required. This result is in accord with the fluorine atom (the functional center) acting as an $-R$ group, i.e., conjugating with $+R$ substituents. It is therefore significant that resonance contributions to δ_p^F values for $-R$ substituents (i.e., $1.88\sigma_R$) follow the σ_R resonance scale. Apparently the F atom is not a sufficiently strong $-R$ group (in contrast to the O^- group—see previous section) to appreciably "level" the order of $-R$ substituents as exhibited in the σ_R scale.

The correlation also appears to offer a "proof" that there is no appreciable direct resonance interaction between *m*-substituents and the carbon atom bearing the functional center, the observed *meta*-resonance effects on reactivity being the result of inductive transmission of charge from the positions ortho to the carbon atom bearing the side-chain functional group.

The $\delta_p{}^F$ values indicate that shielding effects are only $0.58/1.88$ ($=0.3$) times as susceptible to σ_I as to σ_R values. If resonance contributions to $\delta_m{}^F$ values were inductively transmitted, it would be reasonable to expect that the $\delta_m{}^F$ values would be on the order of ($\frac{1}{3}$) (0.3) or 0.10 as susceptible to σ_R values as are the corresponding $\delta_p{}^F$ values. If, however, the *meta*-resonance effects were the result of a direct resonance interaction, both $\delta_m{}^F$ and σ_m values might be expected to have the usual one-third reduction factor in their susceptibilities to σ_R values compared to those for $\delta_p{}^F$ and σ_p values, respectively. In this second instance, the expected susceptibility factor for $\delta_m{}^F$ values to σ_R values would be $\frac{1}{3}(1.88)$ or 0.63. Within the precision of the correlation, the dependence of $\delta_m{}^F$ values on σ_R is zero, a result corresponding more nearly to the former expectation.

Electrophilic reactivities of benzene derivatives (σ^+ Values).—The reactions in this category are characterized as involving in one state of the measured process a distinctly electron-deficient reaction center. It has been widely demonstrated that the Hammett linear free energy relationships for this type of reactivity do not apply for $-R$ *para*-substituents (54 to 63).

Brown & Okamoto (61, 63) have used the effects of m- and p-substituents on the rate constants for solvolysis of phenyl dimethylcarbinyl chlorides to define "electrophilic" substituent constants, σ^+, by the relationship: $\sigma^+ \equiv \log (k/k_0)/(-4.62)$. *Meta*- and $+R$ *para*-substituents follow a satisfactory Hammett linear free energy relationship, for which $\rho = -4.62$. The deviations for $-R$ *para*-substituents are in the direction expected for important resonance stabilizations of the electron-deficient incipient carbonium-ion transition state. The σ^+ values for these substituents therefore reflect a higher-order dependence than σ values on resonance interaction.

A number of relatively precise linear free energy relationships for electrophilic reactivities of m- and p-substituted benzene derivatives have been reported in terms of correlations with σ^+ values (11, 20, 61, 63). It is proposed (61, 63) that σ^+ values will generally suffice to quantitatively correlate and predict reactivities of this type.

A serious limitation to the treatment of Brown is that $-R$ substituents have been represented by only halogen, methyl, and methoxygroups, and only for the latter substituent is the σ^+ markedly different from the σ value. Two electrophilic reaction series are not adequately correlated by σ^+ values (55, 58).

The σ^+ treatment has been extended to include a much wider range of $-R$ *para-substituents* (62). The agreement between σ^+ values calculated for several electrophilic reactivities is not highly precise. Thus, σ^+ values range for p-OCH_3 from -0.64 to -0.82; for p-$N(CH_3)_2$ from -1.49 to -1.87; for p-Cl from $+0.01$ to $+0.23$; and for pC_6H_5O from -0.28 to -0.63. Since the values of ρ^+ range from -2.5 to -13.1, these variations in σ^+ values correspond to deviations in $\log K$ values of from 0.5 to 4.5. It thus appears that the σ^+ treatment of electrophilic reactivities leaves something to be desired from a quantitative standpoint.

Steric inhibition resonance.—Wepster (64) has found relatively precise linear relationships between the physical properties, ultraviolet extinction coefficients (or oscillator strengths), and molar polarizations, and the reactivities, acid strength, and alkaline deacylation rates, for a series of substituted *p*-nitroanilines and *p*-nitroacetanilides in which bulky alkyl substituents inhibit the resonance interaction of the nitro group.

Based upon such a linear relationship and the assumption that complete inhibition of resonance would reduce the extinction coefficient to approximately zero, it is estimated (64) that a completely resonance-inhibited *p*-NO_2 group would increase the acidity of anilinium ion (in H_2O, 25°) by only 1.8 log units compared to the 3.6 log units increase observed for *p*-nitroanilinium ion. This prediction has been confirmed (65) from the consideration that complete inhibition of resonance of the nitro group should change the Hammett σ value to that for the inductive substituent constant, σ_I, i.e., the expected increase in acidity is given as log $(K/K_0) = \sigma_I\rho = (+0.63)(+2.8) = +1.8$.

An estimate of the fractional steric inhibition of resonance of a group is obtained (64) from the quantity, $\epsilon° - \epsilon/\epsilon°$, where, for example, ϵ is the maximum extinction coefficient for 4-amino-2, 6-dimethylnitrobenzene and $\epsilon°$ is that for *p*-aminonitrobenzene. Essentially the same values for the fractional inhibition of resonance of NO_2, $N(CH_3)_2$ and OCH_3 groups, are obtained (64, 65) from reactivities which follow the $\sigma\rho$ relationship by use of the quantity, $\sigma_R° - \sigma_R/\sigma_R°$, where $\sigma_R = \sigma - \sigma_I$ refers to the resonance-inhibited group and $\sigma_R° = \sigma° - \sigma_I$ refers to the "uninhibited" group.

Hyperconjugation effects of m- and p-alkyl substituents.—The effects of methyl, ethyl, i-C_3H_7 and t-C_4H_8 groups in both the *m*- and *p*-positions on the rates of solvolysis of phenyldimethylcarbinyl chlorides in 90 per cent aq. acetone at 25°C. have been investigated (66). The small increase in rates observed for the *meta*-substituents (H, 1.00; *m*-Me, 2.00; *m*-Et, 1.94; *m*-iPr, 1.87; *m*-t-Bu, 1.85) is attributed primarily to the inductive effect ($\sigma_I\rho$ predicts regular increases of rate by factors from about 1.5 to 2.1), with a small contribution from indirectly transmitted hyperconjugation effects. The much larger effects of *para*-substituents (H, 1.00; *p*-Me, 26.0; *p*-Et, 22.0; *p*-i-Pr, 18.8; *p*-t-Bu, 14.4) are attributed primarily to hyperconjugative stabilization by the alkyl groups of the electron deficient center of the incipient-carbonium ion transition state. Within the limits of experimental error, the entropies of activation are constant for the entire series. Brown *et al.* estimate from these results that each α C—H bond of a *para* alkyl group contributes 0.50 kcal. to the stability of the transition state, whereas each α C—C bond contributes 0.40 kcal. A study of the effects of *m*- and *p*-alkyl substituents on the rates of solvolysis of benzhydryl chlorides in aqueous ethanol and aqueous acetone solutions at 0° has also been reported (67). Although the gross aspects of these results are very similar to those of Brown *et al.*, substituent effects are shown to depend to some extent upon solvent.

RESONANCE EFFECTS IN THE ALIPHATIC SERIES

Hyperconjugation effects.—The correlation of the effects of unconjugated substituents, R, on the enthalpies of gas-phase hydrogenation of *trans*-substituted olefins,
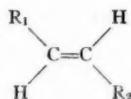
and on the free energies of hydrogenation of aldehydes and ketones, $R_1R_2C = 0$, in toluene solution by the following equation has been reported (68): $\Delta\Delta H°$ (or $\Delta\Delta F°$) = $(\Sigma\sigma^*)\rho^* + (\Delta n)h$. The equation had been previously applied (69) to the acid-catalyzed rates of hydrolysis of unconjugated acetals and ketals. It is assumed that the thermodynamic properties are approximated by the sum of hyperconjugation ($h\Delta n$) and inductive effects (($\Sigma\sigma^*)\rho^*$) which are obtained by considering that the former are approximately linear with the total number of α-hydrogen atoms, n, and the latter are approximately linear with the sum of the σ^* values for the substituents R_1 and R_2.

It is maintained (68) that inductive electron-withdrawal is expected to favor hydrogenation because of the greater electron demand made at the double bond by the atoms in the sp^2 valence state than for the sp^3 state which results on hydrogenation (42). The more negative ρ^* value for hydrogenation of the carbonyl compounds (-6.39) than olefins (-2.41) is attributed to a significant contribution from the form,

In contrast to the ρ^* values, the hyperconjugation parameter, h, appears to be nearly the same for olefin hydrogenation ($h = 0.44 \pm .05$) as for the carbonyl reductions ($h = 0.54 \pm .06$). Similar results are obtained for resonance energies of conjugation (cf. section on Conjugation effects.) The h parameter is taken as the average amount of hyperconjugation stabilization (in kcal.) due to a single α-hydrogen atom in an olefin, aldehyde, or ketone.

The assumed linear dependence of the total observed hyperconjugation effect on the number of α-hydrogens (independent of its environment in the molecule) and the neglect of C—C hyperconjugation are limitations of the treatment. Two independent lines of evidence have been presented (70, 71) indicating that the hyperconjugative effect of a C—H bond is not entirely independent of the nature of other substituents on the carbon atom. A new model for theoretical consideration of hyperconjugation by the LCAO-MO method has been presented (72). The results are in approximate accord with those obtained by the above correlation procedure.

Conjugation effects.—Estimates of extra resonance energies of conjugation of α, β-unsaturated substituents in aldehydes, ketones and *mono-* or

trans-disubstituted ethylenes have been obtained (73) from the difference between observed free energies or enthalpies of hydrogenation and the sum of the polar and hyperconjugation effects calculated from the quantity $(\Sigma\sigma^*)\rho^* + (\Delta n)h$. The values of ρ^* and h used are those determined by the correlations for unconjugated substituents.

The results show the following systematic relationships to structure: (*a*) substitution of a

$$CH_3CH{=}CH{-},\ \ C_6H_5CH{=}CH{-},\ \ C_6H_5{-},\ \ \overset{\overset{\displaystyle H}{|}}{-C}{=}O,\ \ \overset{\overset{\displaystyle O}{\|}}{-C}{-}OC_2H_5\ \text{group}$$

$$\text{at a}\ -\overset{|}{C}{=}\overset{/}{\underset{/}{C}}{-}\ \text{or}\ \overset{\backslash}{\underset{/}{C}}{=}O\ \text{bond}$$
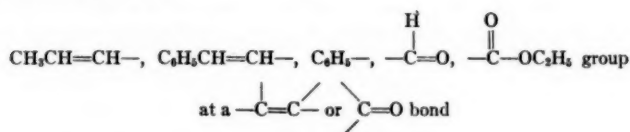
leads to about 6 kcal. of extra resonance energy; (*b*) substitution of two such α, β-unsaturated substituents at the

$$\overset{\backslash}{\underset{/}{C}}{=}O\ \text{bond, or }trans\text{ in the}\ \overset{\backslash}{\underset{/}{C}}{=}\overset{/}{\underset{\backslash}{C}}\ \text{system,}$$
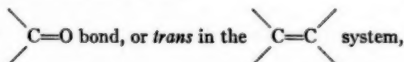
leads to about 11 kcal. of extra resonance energy; (*c*) the extra resonance energy of *mono*-conjugation of an α, β-unsaturated substituent is approximately ten times greater than the value for the average hyperconjugation energy of an α hydrogen atom.

These generalizations are unique for obtaining resonance energies by correcting the observed thermodynamic properties for polar effects. In fact, according to this method the polar contribution to the observed free energies of hydrogenation of the carbonyl compounds is frequently so large as to mask the contributions of hyperconjugation and conjugation. Each of the three generalizations has been correlated by the results of calculations based upon the LCAO-MO method.

A diametrically opposed interpretation of the enthalpies of hydrogenation of olefins has appeared (74). Resonance stabilization is considered to be of no importance in molecules such as butadiene or propene, for which only one unexcited structure can be written. Instead, the effects of σ-bond compression on the change between the sp³ and sp² valence states are considered to be of overriding importance.

STERIC EFFECTS ON SOLVATION

Hall (75) has made an extensive investigation of the relationship between the base strengths of unconjugated amines, $R_1R_2R_3N$, in aqueous solution and the sum of the σ^* values for the groups R_1, R_2, and R_3. A plot of pK_a vs. $\Sigma\sigma^*$ reveals linear relationships defined according to the three classes: primary, secondary, and tertiary amines. These lines (each covering a basicity range of about six powers of ten) are of nearly parallel slope ($\rho^* = 3.2 \pm .1$), and lie successively towards weaker base strength with the following incre-

ments in intercepts: $NH_4^+ \rightarrow RNH_3^+$, $\Delta pK_a = +0.6$; $RNH_3^+ \rightarrow R_2NH_2^+$, $\Delta pK_a = +1.1$; $R_2NH_2^+ \rightarrow R_2NH^+$, $\Delta pK_a = +2.5$. For tertiary amines the correlation with $\Sigma\sigma^*$ appears to be independent of the steric requirements of the R groups. For primary and secondary amines, deviations toward weaker base strength are observed for R groups with large steric requirements.

These results are in accord with the theory of Trotman-Dickenson & Bell (76, 76a, 77) and of Pearson (78, 78a, 78b) which has been supported by others (79, 80) that the base strength of amines in aqueous solution is strongly dependent on the hydration of the ammonium ions through the hydrogen bonding:

$$-\overset{\displaystyle |}{\underset{\displaystyle |}{N}}{}^+\!-H\cdots\cdot OH_2.$$
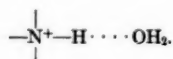
The fact that the correlation equation apparently holds for any tertiary amine is not in accord with Brown's B-strain theory (81, 81a). According to this theory, bases are expected to become increasingly weaker with increasing steric requirements of the groups on the central nitrogen atom, and consequently the effect of B-strain is expected to be the greatest for the tertiary amines. Hall suggests that tertiary ammonium ions are so poorly solvated that steric effects on solvation are nearly constant for this class.

The results of Hall also provide compelling support for the conclusion (3d) that the carboxylic acid acidity order:

$$H_3N^+CH_2CO_2H < CH_3N^+H_2CH_2CO_2H < (CH_3)_2N^+HCH_2CO_2H$$
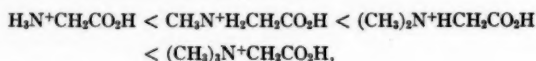
$$< (CH_3)_3N^+CH_2CO_2H,$$

results from the hydrogen bonding,

$$-{}^+\!\overset{\displaystyle |}{\underset{\displaystyle |}{N}}\!-H\cdots\cdot OH_2,$$
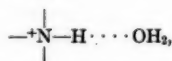
which lowers the effective electron-withdrawing power of the ammonium ion groups. Actually, the pK_a's of $(CH_3)_3N^+CH_2CO_2H(+1.8)$ and $(CH_3)_2N^+HCH_2CO_2H(+1.9)$ are nearly equivalent, whereas that for $H_3N^+CH_2CO_2H(+2.3)$ is distinctly higher—a sequence which is in obvious accord with Hall's conclusions.

A convincing argument has also been presented (64) that steric inhibition of solvation of the ionic form is the main cause of the relatively low base strengths in water of o-alkyl substituted aromatic amines and α-alkyl substituted pyridines.

INTRAMOLECULAR STERIC EFFECTS

The effects on rate of unconjugated R groups of widely varying polar and steric requirements in the sodium methoxide-catalyzed rates of methanolysis of a series of l-menthyl esters, $RCO_2C_{10}H_{19}$, are correlated (82) by the equation: $\log (k/k_0) = \sigma^*\rho^* + \delta E_S$. E_S is a steric substituent constant

obtained by the presumed evaluation of steric effects in the rates of hydrolysis of esters (2g). Evidence is presented indicating that the relatively precise fit is not an accident of an equation with the two adjustable parameters.

The results provide an example of a linear steric energy relationship (83), i.e., $\log (k/k_0) - \sigma^*\rho^* = $ steric effect $= \delta E_s$. A limitation of the treatment is that any hyperconjugation (73) or entropy of solvation effects (84) on rate are included within the steric effect term.

In a similar study (85) on the rates of aqueous alkaline hydrolysis of N-methylanilides, $RCON(CH_3)C_6H_5$, both second and third order rate constants were observed (in excess hydroxide, the pseudo first order constant, $k_1 = k_2(OH^-) + k_3(OH^-)^2$). The effects of unconjugated R groups on k_2 or on k_3 are not adequately correlated by the equation used for the ester methanolysis rates. The following equation, however, is obeyed: $\log (k_3/k_2) = (1.58)\sigma^* + (0.71)E_s + 0.43$. An explanation involving steric inhibition of resonance in the anilide is offered.

ANCHIMERIC ASSISTANCE

Streitwieser (86) has found that the rates for solvolysis reaction series which may be assumed to involve essentially constant steric and resonance effects, follow the equation, $\log (k/k_0) = \sigma^*\rho^*$, if substituents do not enhance the rate by anchimeric assistance. A measure of the driving force for anchimerically assisted rates is taken as the ratio of the observed rate constant to that for the hypothetically unassisted process which is obtained from the quantity $\sigma^*\rho^*$. The procedure does not differ in principle from that applied earlier by Winstein *et al.* (87, 87a).

Retention of configuration (a frequent stereochemical consequence of nucleophilic substitution involving anchimetric assistance) has been found to accompany the solvolysis of trans-4-methoxycyclohexyl *p*-toluenesulfonate in acetic acid and a rate enhancement by a factor of 5 to 7 is indicated by the Streitwieser procedure (88). It is proposed that the solvolysis involves participation by the 4-CH_3O group to give a 5-membered ring oxonium ion intermediate in which the ordinary chair conformation is converted to the boat conformation and two inversions accompany the solvolysis. On the other hand, the acetolysis and formolysis of both methyl *cis*- and *trans*-3-tosyloxy-cyclohexanecarboxylates are normal, involving no rate acceleration and products which are a mixture of olefins and the inverted acetates (89).

The rates of solvolysis of ω-methoxyl-1-alkyl *p*-bromobenzene-sulfonates in ethanol, acetic acid, and formic acid, have been examined (90). The rates of solvolysis of other primary bromobenzenesulfonates, RCH_2OBs, involving a variety of polar groups have also been determined in these solvents and correlated with typical precision by the equation: $\log (k_R/k_{CH_3}) = a + \sigma^*\rho^*$. For the rates at 75°C., the values of ρ^* and a (presumably a steric effect) are for: (a) ethanol, -1.03; -0.37; (b) acetic acid, -1.39, -0.33; and (c) formic acid, -1.45, -0.30, respectively.

It is found that CH_3O-5 and CH_3O-6 (the symbolism CH_3O-n denotes the ring size, n, of the cyclic oxonium ion transition state) involve substantial participation (in log units of rate the enhancement factors are, for EtOH, AcOH, and HCO_2H, respectively: CH_3O-5, $+1.3$, $+2.6$, $+2.8$; CH_3O-6, $+0.4$, $+1.7$, $+1.5$), but negligible participation is involved for CH_3O-3, CH_3O-4, or CH_3O-7.

AROMATIC SUBSTITUTION

Several developments have occurred in the area of aromatic substitution in the brief period since the review of Nelson *et al.* (91).

The Hammett structure-reactivity ($\sigma\rho$) relation has been accommodated to electrophilic aromatic substitution. The rates of aromatic substitution reactions fail to give linear plots of log k vs. σ when the usual Hammett σ values are used. However, it is found that linear plots are obtained when log k for aromatic substitution reactions is plotted against σ^+ values (cf. section on benzene derivatives). The aromatic substitution reactions which have been correlated (61 to 63) with σ^+ are aromatic halogenation, aromatic nitration, protonolysis of aryltrimethylsilanes and the cleavage of aryltrimethylsilanes by bromine (20).

The rates of chlorination for a series of nine polycyclic aromatics parallel their rates of nitration (92). This result suggests that it may be possible to treat polycyclic aromatics as substituted benzenes and assign σ^+ values.

The quantitative relation, log (p_f/S_f) = constant, has been further verified (93). The term p_f is defined as the rate constant for substitution in the *para*-position of a given monosubstituted benzene, divided by one-sixth of the rate constant for the same substitution reaction on benzene. The term S_f equals log (k_p/k_m), where k_p and k_m are the rate constants for substitution in the *para*- and a single *meta*- position (one-half the total rate of *m*-substitution). The ratios k_p/k_m and p_f/m_f are identical by definition.

Similar relations hold for the *meta*- and *ortho*-positions, i.e., log (m_f/S_f) and log (o_f/S_f) equal constants (93). With the *ortho*-position, the relation is valid only if steric effects are negligible.

More data have appeared on the kinetics of the Friedel-Crafts alkylations which are consistent with a rate equation first order in the aromatic, the alkyl halide and the catalyst (MX_3 or M_2X_6). The systems studied have been benzyl chlorides plus aromatics in nitrobenzene with $AlCl_3$ catalyst (94); benzene and toluene with methyl and ethyl bromide in 1,2,4-trichlorobenzene with an $AlBr_3$ catalyst (95); and benzene and toluene with RBr (R = methyl, ethyl, *n*-propyl, *i*-propyl and *t*-butyl) in excess benzene or toluene as solvent with a $GaBr_3$ catalyst (96). In this last series the rates vary by a factor of 10^6 and the rates increase in the order of R groups listed, methyl slowest and *t*-butyl fastest.

The catalytic effect of water in these reactions continues to be verified. The reaction of cyclopropane or propene with benzene or toluene has been studied in detail (97). The solvent was nitromethane and the catalyst was

AlCl₃. Addition of water sharply increased the rate, a maximum rate being achieved when the mol. ratio of $AlCl_3/H_2O$ was about 1.3. Addition of further water decreased the rate until a constant rate was achieved at ratios of 0.6 to 0.35. The reaction mixture was no longer homogeneous at ratios less than 0.35 (97).

In the isomerization of *cis*- to *trans*-2-butene, a maximum rate was obtained when the mol. ratio of BF_3/H_2O was 2 (98).

The exact function of water in catalyzing these reactions is not clear. It is well-accepted that these reactions involve transition states with a high degree of charge separation. Such charge separation can exist only by virtue of large solvation energies, and a reasonable explanation is that water in whatever form it exists serves such a solvating function. Another possibility is that the reactions are specifically catalyzed by H^+ and water serves as a source of protons. Two arguments against this latter possibility are (*a*) it is not clear why HCl is so much less effective than water (97) and (*b*) it is not readily apparent why H^+ is necessary for the alkylations using alkyl halides.

Further work on applying acidity function theory to rates of aromatic nitration (99) corroborates earlier work and supports the currently accepted mechanism that nitration in mixed acid occurs by attack of NO_2^+ on the aromatic. The agreement with acidity function theory is not yet completely satisfactory, a situation that will be clarified by determination of the activity coefficient behavior of nitric acid (99). The fact that certain aromatic nitrations are demonstrably reversible has been corroborated (100).

A large amount of literature has rather suddenly appeared indicating that both electrophilic and nucleophilic aromatic substitution reactions are quite generally two-step processes. The evidence in the case of nucleophilic aromatic substitution has been summarized by Bunnett and co-workers (101). Related to this are the nucleophilic substitution on haloalkenes which appears to proceed through an intermediate in a two-step process (102) and the benzyne intermediates in the reaction of aryl halides with metal amides (103).

With electrophilic aromatic substitution, the fact that the rates of nitration of benzene and tritiated benzene are the same was considered to be in best agreement with a two-step process. The rate-determining formation of the intermediate cyclohexadienyl cation apparently involves little stretching of the C—H bond (104). Using deuterated benzenes, this absence of a kinetic isotope effect was confirmed for nitration (105). Also no kinetic isotope effect was found for the acid catalyzed bromination of benzene in 50 per cent dioxane (106). The fact that phenol iodinates four times as fast as 2,4,6-trideuterophenol was interpreted as a rate-determining formation of product from the cyclohexadienone intermediate (107).

In the conversion of *p*-hydroxybenzenesulfonic acid to *p*-bromophenol with bromine, both spectroscopic and kinetic evidence indicate a cyclohexadienone intermediate. When the *p*-hydroxy group was replaced by amino

or methoxy, the kinetics still indicate an intermediate because addition of bromide ion decreases the rate more than can be accounted for by the formation of Br_3^- ion (108). In the *para*-Claisen rearrangement, the intermediate cyclohexadienone has been prepared and its properties shown to be consistent with those required for an intermediate (109). In the conversion of *o*-cresol to 4-hydroxy-3-methyl-tetraphenyl-methane, an intermediate can be spectroscopically observed (110).

An amazing number of adducts of mesitylene with electrophilic reagents have been isolated as stable salts at low temperature. Salts of the formula $(X \cdot mesitylene)^+BF_4^-$ have been isolated for $X = H$, D, CHO, C_2H_5CO, CH_3, C_2H_5, and C_3H_7 (111). The cations of these salts presumably have the 4-X-1,3,5-trimethylcyclohexadienyl cation structure. The stability of these salts adds support to the concept that cations of this type are true reaction intermediates in at least many electrophilic aromatic substitutions.

A further development has been the preparation of BF_4^- salts of $HAlF_2^+$, $HAlF_4^+$, and $HAlF_6^+$ all of which are fluorinating agents for aromatics (111). Aromatic substitution may also be accomplished using salts of the formula $X^+BF_4^-$ where $X = $ acyl, nitro, nitrosyl, alkyl, and deuterium (111). As extensive as this work appears, it should be noted that only a preliminary account has been published (111).

The cyclohexadienyl cations have actually been known for some time since they are the colored ions formed by treatment of aromatics with hydrogen halides and aluminum halides (112, 112a).

Cyclohexyl, isopropyl and 2-butyl toluenesulfonates have been used to alkylate several aromatic compounds (113). The alkyl group is attached without rearrangement. Even the alkylation of mesitylene with *n*-butyl methanesulfonate gave a 17 per cent yield of butylmesitylenes of which 40 per cent was *n*-butylmesitylene (114). This result was interpreted as indicating that olefins are not intermediates.

The disproportionation of alkylbenzenes has been considered a displacement reaction but the recent carbon labelling experiment of Roberts & Brandenberger (115) indicates that the reaction is more complex than originally supposed. When propylbenzene, labeled on the β-carbon, was treated with $AlCl_3$ for six hours at 100°C., the propylbenzene fraction was 97 per cent *n*-propyl and 3 per cent isopropyl. The surprise was that in the *n*-propylbenzene, the labelled carbon was found to be 25 per cent in the α-position, 75 per cent β-, and 0 per cent γ-.

The disproportionation of ethylbenzene has been studied (116).

Phenols and anilines can be exclusively alkylated in the *ortho*-position using aluminum salts as catalysts (117). No trace of *para*-isomer was detected with ethene and propene. With isobutene and phenol, conditions could not be found which completely eliminated *para*-substitution although the yield of 2,6-di-*t*-butylphenol was good, 74 per cent.

Other unusual orientations in aromatic substitution have been studied.

Cinnamic acid and β-nitrostyrene substitute *ortho* and *para* which has sometimes been explained in terms of resonance structures in which the positive charge is delocalized into the COOH or NO_2 group. Now the ω-styrylammonium ion (in which such delocalization cannot occur) is also found to substitute *ortho* and *para* with only 2 per cent of the *meta*-isomer detected (118). The directing effect of the $N(CH_3)_3^+$ group in aromatic substitution has itself been the subject of discussion (119).

The lack of sulfonation and acylation of anthracene and phenanthrene in the 9-position is due to rapid reversible substitution at that position followed by slower substitution at other positions (120).

The acetylation of 4-*t*-butyltoluene can give either 2-methyl-4-*t*-butylacetophenone or 2-methyl-5-*t*-butylacetophenone depending on the order of mixing reactants. The latter product is formed by isomerization of 4-*t*-butyltoluene to 3-*t*-butyltoluene which is then acetylated. The yield is 93 per cent even though only 67 per cent of the 3-isomer is present at equilibrium. The explanation is that the 3-isomer acetylates more rapidly and the equilibrium shifts to the more reactive isomer (121).

The H—D exchange on phenylacetamide catalyzed by Raney nickel occurs at all positions (122). The difference between inter- and intramolecular aromatic substitution has been reviewed (123). In addition to the direct fluorination of aromatics (111), direct diazotization has been successful with most benzene derivatives (124).

Related to aromatic substitution is the type of bonding in the ferrocene type compounds (125, 125a) since such types of bonding may occur in intermediates and transition states in aromatic substitution. Also substitution reactions on ferrocenes (126, 126a) are a type of aromatic substitution.

The rearrangement of quaternary salts of benzyl amine to give O-alkylbenzyldialkyl amines is a type of aromatic substitution (127, 127a). It has been applied in a novel way to the quaternary ion, N,N-dimethyl-2-phenyl piperidinium, to form a compound containing a nine-membered ring fused to a benzene ring, N-methyl-3,4-benz-1-azacyclononane (128). By studying this type of reaction with *ortho*-substituted benzylamines, intermediate methylenecyclohexadienes have been isolated and colored ions appear which presumably have cyclohexadienyl carbanion structures (129). Both of these may be intermediates in the usual *ortho*-substitution-rearrangement reaction.

The relative reactivities of substituted toluenes towards substitution by chlorine atoms follow a linear $\sigma\rho$ plot, although a discrepancy exists in the ρ value reported by two different groups of workers (15). Further work on the displacement by chlorine atoms of substituent groups on benzene rings has been reported (130).

ACIDITY FUNCTIONS

The H_0 and related acidity functions have been the subject of a number of papers this year, including two reviews by Paul & Long (131, 132). These

reviews have partially summarized work for 1957, so that this report will be restricted to subsequent work. In addition, an attempt will be made to evaluate the current status of acidity function theory.

Values of H_0 have been measured in several new media: 0–100 per cent HF (133, 134), 64–72 per cent $HClO_4$ (135) and solutions of sulfuric acid in acetic acid (6). The H_+ function has been measured from 30–55 per cent and 75–95 per cent sulfuric acid and found to parallel the H_0 function, $dH_+ = dH_0$ (136).

Kinetic data which obey Equation 1, $d \log k = -dH_0$, continue to be reported for a remarkable number of reactions. The derivatives in equation 1, as well as in all following equations, are taken with respect to any function of acid concentration, the per cent acid being generally the most convenient. The reactions recently reported are the O^{18} exchange on t-butyl alcohol in aq. H_2SO_4, $d \log k/-dH_0 = 1.2$ from H_0 equal $-.2$ to -1.9 (138); dehydration of t-amyl alcohol in aq. H_2SO_4, $HClO_4$ and HNO_3, 1.00 from $-.6$ to -1.9 (138); esterification of ethanol with H_2SO_4 in aq. H_2SO_4, 0.96 from -4.3 to -6.9 (139); esterification of 2,4-dinitrobenzyl alcohol with H_2SO_4 in aq. H_2SO_4, 0.96 from -4.9 to -7.0 (140); depolymerization of paraldehyde in aq. HCl, 1.16 from 1.0 to $-.6$ (141); depolymerization of paraldehyde in 45 per cent ethanol with HCl, 1.09 from 1.5 to $-.5$ (141); decomposition of 1,1-diphenylethyl azide in H_2SO_4-acetic acid, 0.83 from -2.1 to -3.2 (6); rearrangement of pinacol to pinacolone in aq. H_2SO_4, 1.00 from -2 to -6 (142); the rearrangement of 2-methyl-1,2-propanediol to 2-methylpropanal in aq. $HClO_4$, 1.33 from $-.2$ to -1.8 (143); the hydrolysis of methoxymethyl acetate in aq. HCl, 1.15 from 1.0 to -1.6 (144); the hydrolysis of ethoxymethyl acetate in aq. HCl, 1.15 from 1.0 to $-.7$ (144); the hydrolysis of methoxymethyl formate in aq. HCl, 1.00 from 1.0 to $-.7$ (144); rearrangement of hexamethylacetone to 3,3,4,4-tetramethyl-2-pentanone in aq. H_2SO_4, 1.28 from -6.1 to -7.6 (145); dissociation of 3,3,4,4-tetramethyl-2-pentanone in aq. H_2SO_4, 1.0 from -7.1 to -7.9 (145) and the hydrogen-deuterium exchange on D-benzene, 1.0 from -7 to -9, 2-D-toluene, 1.0 from -5 to -7, and D-p-xylene, 1.0 from -5 to -6, all in aq. H_2SO_4 (146).

The following reactions were studied at 82–100°C. and it was assumed the dH_0 values were the same as at 25°C.: the hydrolysis of methyl mesitoate in aq. $HClO_4$ and aq. H_2SO_4 (147); the rearrangement of 2-methyl-1,2-propanediol to 2-methylpropanal by H_2SO_4 in 25 per cent by volume dioxan (148); the conversion of 2-methyl-2-propene-1-ol to 2-methylpropanal by H_2SO_4 in 25 per cent by volume dioxane (148); and racemization and O^{18} exchange on 2-butanol in aq. $HClO_4$ and aq. H_2SO_4 (137).

Brief preliminary accounts have indicated that the following reactions obey equation 1: depolymerization of paraformaldehyde (149), dehydration of 4-(p-methoxyphenyl)-4-hydroxy-3-methyl-2-butanone (150), condensation of benzaldehyde with either acetophenone or 2-butanone (150), polymerization of isobutene (151), the Prins reaction between olefins and formaldehyde (152) and the hydrolysis of phthalamic acid (153).

For several reactions it has been reported that the kinetics follow Equation 2, $d \log k = d \log C_{H_3O^+}$. These are the hydrolysis of several amides (154), the hydrolysis of thioacetamide (155) and the hydrolysis of CH_3HgI (156).

The definition of the acidity function, H_0, is $H_0 \equiv pK_{BH^+} + \log (c_B/c_{BH^+})$, where B represents a series of neutral bases, mainly substituted anilines. The definition of the acidity function, C_0, is $C_0 \equiv pK_R^+ + \log C_{ROH}/C_R^+$ where R represents a series of arylmethyl groups (157).

The equations defining H_0 and C_0 are applicable to series of compounds for which the $d \log (f_B/f_{BH^+})$ and $d \log (f_{ROH}/f_R^+)$ are independent of the structure of B and R respectively. These relations have only been demonstrated for water-strong acid systems. Also these relations have only been directly demonstrated for B equal a series of substituted anilines and aryl ketones and R equal arylmethyl groups.

The application of acidity functions to kinetics rests on the Brönsted relation between rate constants and activity coefficients (1b). The relations can be expressed in particularly concise form using derivatives (158).

$$\text{Type I}: S + H^+ = SH^+ \xrightarrow[(+A)]{\text{r. d.}} \text{products}$$

$$d \log k = - dH_0 + d \log (f_A f_B f_{BH^+}/f_B f^*) \qquad 3.$$

$$\text{Type II}: SOH + H^+ = H_2O + S^+ \xrightarrow[(+A)]{\text{r. d.}} \text{products}$$

$$d \log k = - dC_0 + d \log (f_B f_{SOH} f_R^+/f_{ROH} f^*) \qquad 4.$$

A necessary requirement for the validity of Equations 3 and 4 is that the reactant exists primarily in the unprotonated S form for Equation 3 and the SOH form for equation 4. As the acidity is increased, eventually S will exist predominantly in the SH^+ form and no further acid-catalysis will be observed. An intermediate region necessarily exists where $d \log k$ values change from $-dH_0$ to zero, leading to deviations from Equation 1. An analogous situation exists with Equation 4.

Because of the frequent applicability of Equation 1, it has become rather standard practice to regard the activity coefficient terms in Equation 3 as insignificant. Several observations show that this procedure can lead to serious error. From 10–60 per cent H_2SO_4, the term $d \log (f_B f_R^+/f_{ROH} f_{BH^+})$ can be equal to $-dH_0$ itself (157, 158) and a number of reactions of Type I can be found for which the activity coefficient term in Equation 3 is of this form (158). An example which appears to be approaching this behavior is the O^{18} exchange and racemization of 1-phenylethanol in 0.02 to 0.8 M $HClO_4$ where $d \log k$ has values between $-dH_0$ and $-dC_0$ (159).

Another observation is that many reactions of Type I follow Equation 2 rather than equation 1. Such a result is necessarily due to a significant activity coefficient term in Equation 3 (158).

These deviations from Equation 1 anticipate that $d \log (C_B/C_{BH^+})$ for certain $B + H^+ = BH^+$ equilibria will not equal $-dH_0$.

A frequent and questionable use of the H_0 acidity function has been made in connection with a tentative hypothesis suggested by Zucker & Hammett (160). Although these authors never pursued this suggestion further, and even expressed doubts regarding its generality, it has been widely adopted (132).

Briefly it was found that several hydrolysis reactions of Type I followed Equation 2 instead of Equation 1. These reactions have all been conducted in aqueous solutions of strong mineral acids which are sufficiently dilute so that $d \log a_{H_2O}$ is negligible compared to other factors. The subsequent discussion is strictly limited to these conditions. The reactions following Equation 2 were believed to contain an added water molecule in the transition state, so Zucker & Hammett suggested that all reactions following Equation 2 had an added water molecule in the transition state whereas reactions following Equation 1 did not (160).

The greatest objection which has arisen to the Z-H hypothesis is that it leads to contradictory conclusions. In the hydration of 2-methyl-2-butene, equation 1 is followed (138). The Z-H hypothesis would assign to the transition state the composition, olefin $\cdot$ H$^+$. The reverse dehydration under identical conditions of media and temperature also follows Equation 1 (138). The Z-H hypothesis would now assign to the transition state the composition, olefin $\cdot$ H$^+ \cdot$ H$_2$O. Clearly the same transition state has been assigned two different compositions.

In the O^{18} exchange on 2-butanol, Equation 1 is followed and every exchange occurs with inversion (137). The latter observation provides evidence that the reaction involves nucleophilic participation by water in contradiction to the interpretation required by the Z-H hypothesis (159).

As noted above, the reactions of Type I follow Equation 2 because the activity coefficient terms in Equation 3 become significant. Thus, if $d \log f^* = d \log f_{H_3O^+}$, and the other $d \log f$ terms are negligible, Equation 3 reduces to equation 2 (1b).

However, the reduction of Equation 3 to Equation 2 is not necessarily due to the behavior of $d \log f^*$, but can be totally due to $d \log f$ behavior of the reactants, A and S, in Equation 3. In the reversible interconversion of γ-butyrolactone (L) and γ-hydroxybutyric acid (HA) the relation, $d \log(f_L/f_{HA}) = d \log C_{H_3O^+} + dH_0$, is approximately obeyed (161). The transition state for this interconversion appears to be exhibiting no unusual behavior because in the lactone formation Equation 3 reduces to Equation 1 showing that $d \log (f_{HA}f_{BH^+}/f_B f^*)$ is negligible. In fact, this relation coupled with the expression for $d \log (f_L/f_{HA})$ necessarily requires Equation 3 for the lactone hydrolysis to reduce to Equation 2.

The fact that the activity coefficient terms in Equations 3 and 4 can be significant need not discourage the use of these equations. Evidence is accumulating that activity coefficients have certain limiting and predictable behaviors in media in which H_0 and C_0 are valid measures of acidity (157, 158). By determination of f_A, f_S and f_B directly, $d \log (f_{BH^+}/f^*)$ can be evalu-

ated from Equation 3 and this can lead to useful inferences regarding the structure of the transition state, particularly as theories are developed relating structure to activity coefficient behavior.

METHYLENES (CARBENES)

Methylenes (carbenes) have continued (162) to be actively investigated. Methylene, $:CH_2$, from the photolysis of ketene is selective in substitution reactions $RH + :CH_2 \rightarrow RCH_3$, secondary C—H bonds being more reactive than primary (163, 164), in contradistinction to earlier reports of nonselectivity of $:CH_2$ from photolysis of CH_2N_2 (165). These findings have been rationalized by Frey & Kistiakowsky (163) in terms of vibrationally excited $:CH_2$, the less selective $:CH_2$ being in a higher vibrational state. In the presence of inert gases inelastic collisions occur prior to reaction, making $:CH_2$ more selective. Evidence is also presented which leads to the conclusions that "hot" cyclopropane is obtained from $:CH_2 + C_2H_4$. The hot cyclopropane, which decomposes to propylene, readily loses energy by inelastic collisions and thus in the presence of inert gases it can survive without decomposition.

Additional evidence for a very short life for $:CH_2$ has continued to accumulate. Kistiakowsky & Kydd (166) were unable to detect $:CH_2$ with a time-of-flight mass spectrometer connected by short path to flash photolyzed ketene, from which they estimate the reaction probability of $:CH_2 + CH_2CO$ to be $> 10^{-2}$. Davidson & DeMore report that photolysis of CH_2N_2 did not yield detectable quantities of $:CH_2$ among the products trapped in a solid N_2 matrix (167).

Photolysis of methylketene produces ethylidene, $CH_3\overset{..}{C}H$, which disappears by two paths, rearrangement to ethylene and reaction with methylketene to produce C_4H_8 and CO (168). However, isopropylidene, $CH_3\overset{..}{C}CH_3$, from photolysis of dimethylketene rearranges to propylene and is converted to unidentified high molecular weight products, but no tetramethylethylene (169). Since the quantum yield for CO production is unity in the presence or absence of foreign gas, it is postulated that isopropylidene does not react with dimethylketene.

Dichloromethylene, $:CCl_2$ is reported (170) to be a major product from CCl_4 pyrolysis above 1300°C. The dichloromethylene is detected by mass spectroscopy and its I.P. is 13.2 ± 0.2 v. Hine and co-workers (171, 171a, 171b) have continued to make important contributions in their study of the basic hydrolysis of the haloforms. They conclude that $CHClF_2$ and $CHBrF_2$ are hydrolyzed to $:CF_2$ by concerted loss of H and X, since (a) proton exchange with the solvent is observed with all haloforms except $CHBrF_2$ (and presumably $CHClF_2$) and (b) the rate of hydrolysis is greater than the anticipated rate of carbanion formation which is predicted by extrapolation. Evidence is also adduced for (a) a one-step addition of ROH to $:CF_2$ to produce $ROCHF_2$ and (b) the presence of $RO\overset{..}{C}F$ as a reaction intermediate.

The propositions (172) that (a) the presence of methylenes can be detected by their stereospecific *cis*-addition to olefins to produce cyclopropanes and (b) that methylenes are electrophilic, nonradical species continue valid for most of the accumulated information. Acylmethylenes,

$$\underset{\text{RCCH:,}}{\overset{\text{O}}{\overset{\|}{}}}$$

add stereospecifically to *cis*- and *trans*-2-butene (173) as do $:CH_2$, $:CBr_2$ and $:CHCOOC_2H_5$ (172). The original claim that addition of $:CHCOOC_2H_5$ adds in random fashion to methyl sorbate has been revised by the same authors (174). Regarding the electrophilic character, Parham & Wright (175) reported that electron-releasing groups on indene facilitate addition of $:CCl_2$ to the double bond. Etter & Skell (176) find that $:CHCOOC_2H_5$ addition to olefins is also facilitated by electron-releasing groups. However, $:CHCOOC_2H_5$ is less selective than $:CBr_2$. For a test pair of olefins the ratio of rate constants for addition of $:CBr_2$ is 50 and for $:CHCOOC_2H_5$, is 1.8. These properties are rationalized by the hypothesis that methylenes are not "odd" molecules and that they possess orthogonal nonbonding orbitals with two electrons in one oribtal and none in the other. The vacant orbital confers electrophilic, carbonium-like properties on the methylenes, the electrophilicity and the selectivity being inversely modified by resonance involving neighboring atoms (176).

Nonetheless, Gallup (177) reported briefly a LCAO—MO calculation which favors a triplet ground states assignment for CH_2. Radical reactions may accompany methylene reactions. Frey & Kistiakowsky (163) in their study of $:CH_2 + RH$ reactions, suggest ethane is produced in a radical reaction since its formation is suppressed by small additions of oxygen, without affecting the main reactions. Urry, Eiszner & Wilt (178) describe a rapid reaction between CH_2N_2 and CBr_4, CHI_3 and $CHBr_3$, for which they propose a multiple-step radical chain reaction. Although they postulate $:CH_2$ in the initiation step, this is by no means necessary or indicative of radical character of methylenes.

The addition of $:C(COOCH_3)_2$, $C_6H_5\overset{..}{C}CN$ (179, 179a), and $:CHCOOC_2H_5$ (180) to acetylenes producing cyclopropene derivatives has been reported. Conjugated olefins add to the 1.2-positions exclusively, yielding vinylcyclopropanes (181). The synthesis of β-halonaphthalenes from indenes and $:CX_2$ has been extended (175, 182). An acylmethylene has been suggested as an intermediate in the photolytic or silver oxide catalyzed decomposition of

$$\underset{\text{R—C—CN}_2\text{—CH}_2\text{—R} \rightarrow \text{N}_2 + \text{R—C—CH=CH—R (183).}}{\overset{\text{O} \qquad\qquad\qquad\qquad \text{O}}{\overset{\| \qquad\qquad\qquad\qquad \|}{}}}$$
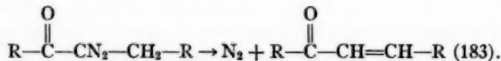
The structure of products obtained from methylenes and aromatic compounds is still controversial, two publications indicating that both norcaradienes and tropilidenes are obtained (184, 185, 186).

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MOLECULAR ELECTRONIC SPECTRA[1]

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INTRODUCTION

The last few years have seen considerable progress in the elucidation of the electronic spectra of diatomic and polyatomic molecules, as is evident from the summaries of Sponer (178), Kasha & McGlynn (82), and Förster (52) in the 1955, 1956, and 1957 volumes of this *Review*. Each of these annual summaries was written from a somewhat different point of view and with somewhat different emphasis as is the custom in the *Annual Review of Physical Chemistry*. In the present report on the year 1957 the emphasis will be on the simpler molecules and on the results of fine structure investigations. For a better understanding, in a few cases some of the older literature will be included in the discussion.

Even though last year's review by Förster called attention to Mulliken's (124) "Report on the Nomenclature for the Spectra of Polyatomic Molecules," it seems appropriate to mention it again since in many recent papers some of the recommendations of this report are not yet accepted. It is obvious that a unified nomenclature for the whole field of molecular spectroscopy is most desirable. It leads to confusion if in a narrow field some authors use a special notation not in conformity with that used in other parts of spectroscopy. Thus, while it has been agreed in the designation of a transition to put the upper state first and the lower second (e.g., the $A - X$ transition of CO, meaning a transition with upper state A and lower state X), many authors still make the order dependent on whether they are considering emission or absorption. Whether the transition is observed in emission or absorption should be indicated by an arrow-head (e.g., $A \leftarrow X$ refers to absorption, $A \rightarrow X$ to emission). Thus one should not talk about $N - V$ transitions but $V \leftarrow N$ transitions if N is the ground state and one is discussing absorption spectra. The notation for diatomic molecular spectra has, of course, long been established, but reference should be made to the revision adopted by the Joint Commission for Spectroscopy as recommended by Jenkins (79).

DIATOMIC MOLECULES

Analyses of Band Systems

During the past year a considerable number of band systems of diatomic molecules have been analyzed. Narasimham (130) discovered the spectra of two molecules previously not found: PH^+ and P_2^+. Both were observed in a hollow cathode discharge through helium which contained a little phos-

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[1] The survey of literature pertaining to this review was concluded December, 1957.

phorus vapour and, in the first case, some hydrogen. For PH^+ a $^2\Delta - {}^2\Pi$ system was found similar to the only known band system of SiH. The $^2\Pi$ state is the ground state. The equilibrium internuclear distance in this state is $r_e'' = 1.425$ A, the first vibrational quantum $\Delta G''(\frac{1}{2}) = 2299.6$ cm.$^{-1}$. Two band systems were found for P_2^+, a $^2\Pi - {}^2\Pi$ system near 3600 A and a $^2\Sigma - {}^2\Sigma$ system near 4100 A. The latter system corresponds to the violet N_2^+ bands. According to recent work by Douglas & Rao (47) on P_2, and contrary to Narasimham's suggestion it seems very likely that the lower state $^2\Sigma_g^+$ of the $^2\Sigma - {}^2\Sigma$ bands is the ground state as in N_2^+. The values $r_e'' = 1.896$ A and $\Delta G''(\frac{1}{2}) = 733.4$ cm.$^{-1}$ are provisional since the vibrational numbering has not been established. The position of the $^2\Pi$ states relative to the ground state is not known.

New data on a number of known hydrides have been obtained: Velasco (191) has observed and analyzed a new absorption system of LiH and LiD. The upper $^1\Pi$ state has a very shallow potential energy curve with $r_e = 2.378$ A, $\Delta G(\frac{1}{2}) = 130.7$ cm.$^{-1}$. Kiess & Broida (83) have measured and analyzed the 0-1 and 1-2 bands of the $^2\Delta - {}^2\Pi$ system of CH which lie near 4890 A, and in this way have obtained improved vibrational constants, e.g., $\Delta G''(\frac{1}{2}) = 2732.8$ cm.$^{-1}$. A band system in the region 4300 to 5500 A, first observed by Schüler & Woeldike (176) and variously assigned to H_2O, OH^-, and OH, was shown by Barrow & Downie (8) to represent a $B^2\Sigma^+ - A^2\Sigma^+$ transition in OH in which $A^2\Sigma^+$ is the upper state of the well-known $^2\Sigma^+ - {}^2\Pi$ bands of OH. The $B^2\Sigma^+ - A^2\Sigma^+$ system has now been analyzed in detail both for OH and OD by Barrow (5). The upper ($B^2\Sigma^+$) state has a very shallow potential energy curve ($r_e \sim 1.80$ A, $\Delta G(\frac{1}{2}) = 660$ cm.$^{-1}$). Some ultraviolet bands first found by Benoist (15) have been shown by Schüler & Michel (174) to have the $A^2\Sigma^+$ state as lower state and thus establish another fairly highly excited state, $C^2\Sigma^+$. However, the analysis is based on low resolution spectra.

A band system similar to the $B^2\Sigma^+ - A^2\Sigma^+$ bands of OH has been observed and analyzed for the iso-electronic HF^+ (and DF^+) by Johns & Barrow (80). The lower state with $r_e = 1.076$ A, $\Delta G(\frac{1}{2}) = 2766.5$ cm.$^{-1}$ corresponds to the $A^2\Sigma^+$ state of OH; the $A^2\Sigma - X^2\Pi$ system involving the ground state of $X^2\Pi$ has not yet been found but, on the basis of electron collision work on the ionization potential [Coope, Frost & McDowell (36)], is predicted to be in the photographic infrared.

The $^2\Delta - {}^2\Pi$ system of SiH has been reinvestigated by Douglas (45). Previously only the $0-0$ and $1-1$ bands had been analyzed. Now enough bands have been analyzed to obtain reliable vibrational constants, e.g., $\omega_e'' = 2042.47$, $\omega_e''x_e'' = 35.67$ cm.$^{-1}$.

An absorption spectrum of GaH (and GaD) was observed for the first time by Neuhaus (132) near 5700 A. The transition is $^1\Pi - {}^1\Sigma$. The B_0 value of the $^1\Sigma$ ground state of GaH is 6.046 cm.$^{-1}$.

A good deal of work has been carried out on the band spectra of N_2. Following the analysis of the fifth positive system $x^1\Sigma_g^- - a'^1\Sigma_u^-$ by Lofthus (106), Lofthus & Mulliken (108) showed, on the basis of new high resolution

spectra, that Kaplan's first and second systems are $y^1\Pi_g - a'^1\Sigma_u^-$ and $y^1\Pi_g - w^1\Delta_u$ transitions, with the first having the lower state in common with the fifth positive group. Much improved rotational and vibrational constants have been obtained. Wilkinson (206) has investigated the Lyman-Birge-Hopfield bands $a^1\Pi_g - X^1\Sigma_g^+$ of N_2 in absorption under high resolution and has obtained improved values for the constants of the upper state. The lower state B_0 value, 1.9808 cm.$^{-1}$, agrees very well with the Raman value of Stoicheff (180). Lofthus (107) has observed and analyzed a large number of new and old singlet bands in the visible and ultraviolet regions using high resolution. In addition to confirming many singlet states already in the literature, he has established two new states: $z^1\Delta_g$ and $k^1\Sigma_u^+$. Mulliken (125) has given a summary of the data on all the known and many predicted states of N_2 and N_2^+.

Until recently the first excited singlet state of the P_2 molecule was believed to be $^1\Sigma_u^+$, the upper state of the ultraviolet bands. However, now Douglas & Rao (47) have observed another singlet system at longer wavelengths (2850 to 3120 A) whose lower state is the ground state and whose upper state is a $^1\Pi$ state and presumably the exact analogue of the $a^1\Pi_g$ state of N_2. This observation indicates strongly that the electronic structure of diatomic molecules containing second period atoms is more closely analogous to those with first period atoms than was thought until now. The analysis of the new bands also leads to improved rotational and vibrational constants of P_2.

The spectra of a number of oxides have been investigated during the past year. A perturbation in the $v = 6$ level of the $A^1\Pi$ state of CO has been studied by Onaka (142). Further analyses of the absorption bands of NO in the vacuum ultraviolet have been made by Barrow & Miescher (11). In addition to much improved constants for the $A^2\Sigma^+$, $B^2\Pi$ and $D^2\Sigma^+$ states, they have obtained evidence of four new electronic states $F^2\Sigma$, $I^2\Pi$, $M^2\Sigma$, and $P^2\Sigma$. The last two of these are in all probability Rydberg states. Ogama & Shimauchi (140) have analyzed an additional β' band of NO in the vacuum ultraviolet as well as two bands of the $B'^2\Delta - B^2\Pi$ transition in the photographic infrared. They give revised values of the rotational and vibrational constants of the $B^2\Pi$ and $X^2\Pi$ states.

Lagerqvist & Selin (97, 98) have studied the spectra of VO. The earlier fine structure analysis of the visible band system by Mahanti (111) was shown to be incorrect. The revised B_e'' value is 0.548$_0$ cm.$^{-1}$ corresponding to $r_e'' = 1.589$ A. The same authors have observed a new infrared band system which was first suggested by a low-dispersion infrared recording of Kleman and Liljeqvist (88). This system is of considerable astrophysical importance [McKellar (115)]. Lagerqvist & Selin (99) have also analyzed several additional bands in the $A^1\Sigma - X'^1\Sigma$ system of SrO and obtained $\omega_e'' = 653.49$ and $\omega_e'' x_e'' = 3.96$ cm.$^{-1}$. Moreover they report a new band system at 11,000 A which, however, has not yet been analyzed. Following the earlier work on the triplet systems of ZrO by Lagerqvist, Uhler & Barrow

(100) and by Uhler (189), the singlet systems A and B have been analyzed by Åkelind (1) and Uhler & Åkelind (190). Both systems are $^1\Sigma - ^1\Sigma$ systems (or possibly $^1\Delta - ^1\Delta$) but have no state in common. Two band systems of TaO have been found and analyzed by Premaswarup & Barrow (150). They are assigned as $^2\Delta - ^2\Delta$ and $^2\Pi - ^2\Delta$. It is not certain whether the common lower state $^2\Delta$ is the ground state. Its r_e value is 1.687 A. The absorption spectra of ClO, BrO, and IO have been studied under high resolution in the flash photolysis of halogen-oxygen mixtures by Durie & Ramsay (50). The observed transitions are $^2\Pi - ^2\Pi$. The internuclear distances in the ground states of ClO and BrO are 1.546 and 1.65 A, respectively.

Only one sulphide has been investigated recently: SiS. Nilheden (138) has greatly extended the analysis of the $D^1\Pi - X^1\Sigma^+$ system and has established three perturbing states with approximate values for their constants.

A number of halide spectra have been analyzed. The ultraviolet absorption spectra of LiCl, LiBr, and LiI have been studied by Berry & Klemperer (17). Only diffuse bands and continua appear just as for the other alkali halides. Onaka (143) has reinvestigated the $A^1\Pi - X^1\Sigma^+$ bands of BF with a vacuum echelle spectrograph and has obtained considerably improved rotational constants; for the ground state $B_e'' = 1.510_7$, $\alpha_e'' = 0.016_5$ cm.$^{-1}$, $r_e'' = 1.265$ A. Naudé & Hugo (131) have analyzed the $B^1\Sigma^+ - X^1\Sigma^+$ and $C^1\Sigma^+ - X^1\Sigma^+$ systems of AlF in the region 1930 to 1690 A, and have in this way for the first time obtained reliable, rotational constants for the ground state of AlF: $B_e = 0.552_3$, $\alpha_e = 0.0048$ cm.$^{-1}$, $r_e = 1.655$ A. These values agree suprisingly well with those derived from $R - Q$ and $P - Q$ head separations by Barrow, Johns & Smith (10). Reddy & Rao (162) have observed six new band systems of AlCl in the region 2075 to 1820 A, which involve six new electronic states. Barrow, Dodsworth & Zeeman (7) have analyzed the rotational structure of the $A^3\Pi_0^+$, $B^3\Pi_1 - X^1\Sigma^+$ systems of GaF, both for the Ga^{69} and Ga^{71} isotopes. They obtained $r_e = 1.775_4$ A for the ground state. The analysis of the $A - X$ system of TlCl by Kadesch, Moldenhauser & Winans (81) was revised by Barrow (6) and now leads to $r_e'' = 2.484$ A in excellent agreement with the microwave value. A number of complex spectra due to MnF, MnCl, and MnBr in the near ultraviolet, blue-green, red, and infrared have been vibrationally analyzed by Hayes & Nevin (58). Bands assigned to ZrF in the literature have been shown to be due to CuF by Carroll & Daly (28). Venkateswarlu & Verma (193) have found and analyzed two new band systems of Br$_2$ in the region 3150 to 2670 A whose common lower state is the upper state $^3\Pi_{0u}^+$ of the well-known visible Br$_2$ bands. Haranath & Rao (57) have observed a new band system each for ICl and IBr in emission in the region 3800 to 4400 and 3800 to 3900 A, respectively. The lower state in each case is the known $^3\Pi_1$ state.

DISSOCIATION AND PREDISSOCIATION

Less work has been done on dissociation energies in the past year than in previous years. This is mainly due to the fact that the controversy with regard to the correct values of $D(N_2)$ and $D(CO)$ is now generally considered

to be settled in favour of the "high" values $[D(N_2) = 9.759$ ev, $D(CO) = 11.108$ ev]. Reflected shock wave studies by Toennies & Greene (188) are in agreement with these values but not with the "low" values. New electron impact experiments by Frost & McDowell (53) confirm the earlier work of Clarke (31) which gave the first definite evidence from electron impact work that it is compatible only with the high $D(N_2)$ value.

The dissociation energies of Cu_2, Ag_2, and Au_2 previously obtained by linear Birge-Sponer extrapolation by Kleman, Lindkvist & Selin (89) have now been more accurately determined by mass-spectroscopic methods by Drowart & Honig (49) and Schissel (171). The former authors have also compared other spectroscopic D values with mass spectroscopic values.

Wilkinson & Mulliken (208) have observed a broadening of the individual lines of the 12−0 Schumann-Runge band of O_2 which they ascribe to predissociation of the $B^3\Sigma_u^-$ state by a $^3\Pi_u$ state. There is also evidence for a continuous absorption corresponding to the direct transition from the ground state to $^3\Pi_u$. Both mechanisms are probably important as primary processes of photochemical dissociation of O_2 above 1750 A. Wilkinson (204) has obtained further evidence for inverse predissociation in the $v' = 3$ level of the $C^2\Sigma_u^+$ state of N_2^+.

The dissociation energy of F_2 as obtained from the heat of formation of ClF and the spectroscopic value for $D(ClF)$ is much lower $[D(F_2) = 1.57$ ev] than corresponds to the long wavelength limit of the absorption continuum of F_2 in the violet and near ultraviolet region. Rees (163) has shown that the intensity distribution in the continuum is compatible with the low $D(F_2)$ value if it is assumed that the upper state is mainly $^1\Pi_u$. Shock-wave studies by Wray & Hornig (210) also support the low value.

In the new spectrum of PH^+ mentioned above, Narasimham (130) has found a predissociation in the $v = 0$ and $v = 1$ levels of the $^2\Delta$ state probably caused by the $^4\Pi$ state arising from normal products. The predissociation gives an upper limit, 3.35 ev, for the dissociation energy. From the extension of the vibrational levels of OH in the $A^2\Sigma^+$ state which resulted from the study of the $B^2\Sigma^+ - A^2\Sigma^+$ bands [see subsection on Analyses of Band Systems], Barrow (6) has obtained an improved value for $D(OH)$ viz., 4.395 ev. The dissociation energies of LiH and LiD, previously known only by a somewhat uncertain extrapolation have been determined with a high degree of precision from the predissociation by rotation observed by Velasco (191) in the new absorption bands discussed above, viz., D_0 (LiH) = 2.4288 ev, D_0 (LiD) = 2.4509 ev. The dissociation energy of SiH has been determined by Douglas (45) to be 3.19 ± 0.25 ev.

Lagerqvist, Nilsson & Barrow (96) have found that a predissociation previously reported in the ground state of AlO is not real and that, therefore, the dissociation energy of AlO is not as low as was claimed. Barrow, Johns & Smith (10) have found a small discrepancy between the spectroscopic value of $D(AlF)$ and the thermochemical value which may have to be explained by a potential maximum in the $A^1\Pi$ state of AlF.

Predissociation has been observed in the upper $^2\Pi$ states of the observed

bands of ClO, BrO, and IO by Durie & Ramsay (50) and the dissociation processes have been discussed. The dissociation energies of the ground states are 2.746 ev, 2.40 ev, and 1.8 ev, respectively.

Watanabe (199) has observed the dissociation limits corresponding to a splitting into positive and negative ions $(X^+ + X^-)$ for Cl_2, Br_2, and I_2, and from a determination of the ordinary ionization potentials of these molecules has derived the dissociation energies $D(Cl_2^+) = 4.01$, $D(Br_2^+) = 3.26$, $D(I_2^+) = 2.74$ ev, which are appreciably greater than those of the corresponding neutral molecules.

The dissociation continua of the alkali halides have been discussed by Berry (16).

FORBIDDEN TRANSITIONS

An outstanding result is the recognition by Wilkinson & Mulliken (209) of an electric quadrupole component of the Lyman-Birge-Hopfield bands of N_2. These bands had previously (60) been shown to be due to a magnetic dipole transition, $^1\Pi_g - ^1\Sigma_g^+$. As for all magnetic dipole transitions a weak quadrupole component is expected, but in no case of an electronic transition had such a component been observed. Wilkinson and Mulliken observed weak S and O branches $(\Delta J = \pm 2)$ which can only result from quadrupole radiation. The only other known case of molecular quadrupole transitions are the rotation-vibration bands of H_2 (61). As already mentioned, Douglas & Rao (47) have recently observed the analogue of the Lyman-Birge-Hopfield bands in P_2 without, however, observing the quadrupole branches.

In addition to forbidden transitions which are rigorously forbidden as dipole radiation, a number of transitions have been studied which are forbidden by various approximate selection rules. The most common ones are the singlet-triplet intercombinations of which the GaF and TlCl bands mentioned earlier are examples, viz., $^3\Pi - ^1\Sigma$. Another example of the same type are the $C^3\Pi_u - X^1\Sigma_g^+$ bands of N_2 recently observed by Tanaka (184). The Vegard-Kaplan bands $A^3\Sigma^+ - X^1\Sigma_g^+$ of N_2 have thus far not been observed in absorption in spite of many efforts. The long life of the $A^3\Sigma^+$ state, thus indicated, has been confirmed by a molecular beam method by Lichten (102). He finds a lower limit of 10^{-2} sec. for this lifetime. A number of intercombinations have been observed recently in CO in addition to the well-known Cameron bands $(a^3\Pi - X^1\Sigma^+)$, viz., the $a'^3\Sigma^+ - X^1\Sigma^+$ bands and the $d^3\Pi - X^1\Sigma^+$ bands [Herzberg & Hugo (64), Hugo (69), and Tanaka, Jursa & LeBlanc (185)]. In addition a somewhat different type, $e^3\Sigma^- - X^1\Sigma^+$, was observed (64) showing branches with $\Delta K = \pm 2$ and 0 only. The rule that Σ^- states do not combine with Σ^+ states does not apply to intercombinations [Schlapp (172)]. More recently Mulliken (126) has suggested that the $d - X$ bands of CO actually represent a $^3\Delta - ^1\Sigma$ transition, i.e., a type not heretofore observed. Recent work by Hugo (69) on the band structure seems to support Mulliken's interpretation.

The only definitely known doublet-quartet intercombinations are the

$^4\Sigma^- - {}^2\Pi$ transitions in GeH and SnH [Kleman & Werhagen (90)]. Attempts to find a $^4\Pi - {}^2\Pi$ transition in NO have failed thus far. Lagerqvist & Selin (98) suggest that the visible VO bands represent a quartet-doublet transition.

The $A\,{}^3\Sigma_u{}^+ - X\,{}^3\Sigma_g{}^-$ bands of oxygen represent still a different type of forbidden transition violating the rule $\Sigma^+ \leftarrow\mid\rightarrow \Sigma^-$. These bands have been extensively studied because of their importance in the night glow. In a recent paper by Barth & Kaplan (12) these bands have been excited in an "air" afterglow and the intensity distribution has been compared with that in the night glow. The reaction $N + O_3 \rightarrow NO + O_2$ may account for the excitation in both cases.

One important case of forbidden transitions made possible by intermolecular interactions is the infrared atmospheric O_2 bands ($^1\Delta_g - {}^3\Sigma_g{}^-$) as observed in liquid O_2 by Cho, Allin & Welsh (30). All but the 0—0 band are found to be affected by double transitions in an $O_2 - O_2$ complex which consist of an electronic transition in one and a vibrational transition in the other O_2 molecule.

INTENSITIES

Extensive work both on the distribution of intensities in the rotational and vibrational structures and on absolute (and relative) absorption intensities of different electronic transitions has been carried out.

Deviations from a Boltzmann distribution were established for the OAH ${}^2\Sigma^+$ state of OH in various flames by Broida & Kostkowski (23). While the population of the low K levels was seen to conform to a temperature calculated from equilibrium considerations, the population of the levels of high K is anomalously high and corresponds to a much higher temperature.

A detailed investigation of the vibrational intensity distribution in the Swan bands of C_2 in a King furnace has been carried out by Phillips (145) and comparisons with theoretical computations have been made. Phillips (146) has also applied the vibrational transition probabilities to the determination of the temperature of an R-type star [see also Wyller (213)]. Further extensive calculations of vibrational intensity distributions have been carried out by Nicholls and his collaborators (133 to 136). For calculations on $O_2{}^+$ see also Rao & Ranade (159). The calculations refer particularly to band systems of importance for aurorae, the night glow, and cometary and stellar spectra. Anomalies in the vibrational intensity distribution in the $b\,{}^3\Sigma^+ - a\,{}^3\Pi$ bands of CO have been studied by Barrow, Gratzer & Malherbe (9). The electron excitation function of the violet $N_2{}^+$ bands has been determined by Stewart (179).

Absolute absorption intensities of a number of gases have been studied in the vacuum ultraviolet by a number of investigators. Lee (101) has determined the absorption coefficients of O_2 in the region 1320 to 200 A. Watanabe & Marmo (200) have investigated both O_2 and N_2 in the region 1500 to 850 A. Weber & Penner (202) have determined absolute intensities of the γ-bands of NO, while Sun & Weissler (182) and Walker & Weissler (195)

have determined absorption coefficients of NO in the region 1400 to 375 A. CO was studied by Sun & Weissler (183) in the region 1310 to 375 A. Some of the continuous absorption spectra studied in these papers correspond to photo-dissociation, others to photo-ionization. In several of the papers quoted the ionization produced has been measured directly, and the ionization potentials and yields have been determined. Results on diatomic molecules have been summarized and extended to Cl_2, Br_2, I_2, HCl, HBr, and HI by Watanabe (199). For results on NO see also Zelikoff & Aschenbrand (215). The low ionization potential of NO (9.25 ev) thus obtained is important for an interpretation of the D layer of the atmosphere since NO appears to be the only conceivable constituent of the upper atmosphere that can be ionized by Lyman alpha radiation [see Nicolet (137)]. The ionization yields in O_2 and N_2 are of importance for an understanding of the E and F layers of the ionosphere.

THEORETICAL WORK

Dalgarno & Lewis (38) have continued their calculations of the wave functions and energies of some of the excited states of the H_2^+ ion by means of a variational method. These calculations show that excited oribitals are much more satisfactorily represented by the united-atom approximation than by the separated-atom approximation. Similar calculations have been carried out by McCarroll & Moiseiwitsch (114) and Moiseiwitsch & Stewart (122) on the HeH^{++} ion, by Moiseiwitsch (121) on the He_2^+ ion, and by Huzinaga (72) for H_2 and He_2. Bates & Carson (14) have given exact wave functions for several states of HeH^{++}, and Dalgarno & Stewart (42) have carried out a perturbation calculation of the $2p\pi$ state of the same molecule. The Belfast group have also carried out extensive calculations of the oscillator strengths of transitions in HeH^{++} [Arthurs, Bond & Hyslop (3); Arthurs & Hyslop (4); Dalgarno, Lynn & Williams (39)] and in H_2^+ [Dalgarno & McCarroll (40)]. For the latter case independent calculations leading to analytical forms for the transition probabilities for any fixed internuclear distances have been carried out by Herman & Wallis (59). Wu & Bhatia (212) Wu (211), and Dalgarno & McCarroll (41) have calculated the effect of the coupling of electronic and nuclear motions on the potential energy at large internuclear distances in H_2^+, H_2, HeH^{++}, He_2, and related systems. While according to the former authors an appreciable correction arises to the ordinary van der Waals interaction, according to the latter authors the effect is appreciable only when one of the separated atoms has nonzero orbital angular momentum.

Hurley (70) has modified Moffitt's (120) method of atoms in molecules by introducing an intra-atomic correlation correction and has applied this method to calculations of the ground states of HF, N_2, and HeH^+. He has thereby obtained energy values for the ground states which agree much better with experiment or, for HeH^+, with exact calculations than Moffitt's original approximation. Bingel (18) has developed an analogue of Moffitt's

method which uses the exact energy levels of the united rather than the separated atoms, while Preuss (151) has combined the advantages of Moffitt's and Bingel's methods and has obtained fairly satisfactory binding energies for H_2^+ and H_2.

Still another modification of Moffitt's method [Fumi & Parr (54)] has been applied to several electronic states of O_2^+ by Bassani, Montaldi & Fumi (13). The excitation energies of the $^4\Pi_u$ and $^2\Pi_u$ states above the $^2\Pi_g$ ground state obtained in this way agree within 0.1 ev with those observed. Without making use of empirical atomic data but using a method otherwise similar to Moffitt and Fumi & Parr, Itoh & Ohno (77) have calculated the positions of the excited states of O_2 and found satisfactory agreement with observation. Arai (4a) has introduced a further modification of Moffitt's method, which he calls the method of "deformed" atoms in molecules.

Without introducing any empirical parameters, Kotani et al. (92) have carried out detailed molecular orbital calculations with configuration interaction for O_2, O_2^+, and Li_2. The introduction of configuration interaction considerably improves the agreement with experiment. Ohno (141) has given the results of similar calculations for the BH molecule and Rahman (154) for the ground state of H_2. Valence bond calculations for LiH and BeH$^+$ have been carried out by Miller et al. (119).

POLYATOMIC MOLECULES

VIBRATIONAL AND ROTATIONAL STRUCTURE OF ELECTRONIC TRANSITIONS

Although the vibrational structures of many band systems of polyatomic molecules have been analyzed in the last three decades, only in the last few years has there been significant progress in the analysis of rotational structures. This work has shown that a change of symmetry of the equilibrium configuration occurs in many electronic transitions of polyatomic molecules. We shall first discuss a number of simple stable molecules.

Simple stable molecules.—The CS_2 molecule was the first linear polyatomic molecule for which a nonlinear structure in the first excited state was suggested [Mulliken (123)] on the basis of a partial rotational analysis [Liebermann (103)]. More recently Kleman (87) has reinvestigated the near ultraviolet CS_2 bands in considerable detail and has definitely confirmed Mulliken's suggestion. The $S-C-S$-angle in the upper state is approximately 140°. Therefore, the molecule in this state represents only a slightly asymmetric top and the band fine structure does not deviate much from that of a molecule that is linear in both electronic states. The nonlinearity of the molecule in the excited state follows: (a) from the presence of a long progression in the bending vibration; and (b) from the observation of K-type doubling in the $\Pi, \Delta, \Phi, \ldots$ type levels of the upper state which combine with corresponding levels of the lower state as "hot" bands ($\Pi-\Pi, \Delta-\Delta, \Phi-\Phi, \ldots$). The magnitude of the doubling is quite considerable for the Π upper levels, much smaller for Δ, and very slight for Φ levels.

Douglas (46) has shown that the lines of the near ultraviolet CS_2 bands show an appreciable broadening in a magnetic field, and that, therefore, the upper state must be a triplet state. Bands at the short end of this absorption region are uninfluenced by the magnetic field and probably belong to a singlet-singlet system.

The C_2H_2 (and C_2D_2) molecule was the first linear molecule for which the nonlinear structure of the first excited state was established in every detail [Ingold & King (73), and Innes (74)]. In particular, in addition to the two criteria given above there is a third very strong point: instead of one progression of hot bands coming from the vibrational level ν_4 (bending vibration) of the ground state there are two, corresponding to $K = 0$ and 2 in the upper state and corresponding to $K' - l'' = \pm 1$. It can be concluded unambiguously that in the upper state the molecule has the transform (point group C_{2h}) and that the upper electronic state is an A_u state. The C—C distance in the excited state is 1.38_8 A as compared to 1.208 A in the ground state.

A very similar situation has been found in HCN [Herzberg & Innes (65)]. All three criteria given above lead unambiguously to the conclusion that in the first excited state (α) the molecule is bent. The H—C—N angle is found to be 125°, the C—N distance 1.297 A, and the C—H distance 1.14 A. From the sign of the K-type doubling it follows that the α state is an A'' state, that is, that the electronic eigenfunction is antisymmetric with respect to the plane of the molecule. Transitions to three further electronic states, β, γ, and δ, have been found at shorter wavelengths. In two of these, β and γ, the molecule is also bent, with an angle of 114.5° and 154°, respectively. The electronic species is A'' and A' respectively. The structure of the molecule in the δ state has not yet been established.

Formaldehyde was the first polyatomic molecule for which a rotational analysis of the ultraviolet absorption was accomplished [Dieke & Kistiakowsky (43)]. However, the detailed interpretation of the spectrum has been a puzzle until last year when, following an earlier suggestion of Walsh (198), Brand (20) and Robinson (167) independently showed that in the upper state the molecule is nonplanar. This assumption makes it possible to understand the vibrational structure of the band system, in particular the existence of two sets of levels in the upper state separated by only 124 cm.$^{-1}$ as shown by the weak α band whose separation from the A band does not agree with any vibrational frequency of the ground state. The frequency 124 cm.$^{-1}$ is assumed to correspond to the doubling which arises on account of the presence of two potential minima for a nonplanar structure. Moreover the rotational structure gives clear indication of nonplanar structure, since the inertial defect $\Delta = I_C - I_A - I_B$ for the upper states of both the α and A bands is negative, while it is always positive for planar molecules (for a large deviation from planar structure I_C is expected to be much less than $I_A + I_B$). The deviation from planarity is estimated to be 20°. At the long wavelength side of the main H_2CO absorption system lie some very weak bands [Brand (20), Cohen & Reid (34), and Robinson (167)] which have been interpreted

by Robinson & DiGiorgio (168) as a transition to the triplet state $(^3A_2)$ corresponding to the singlet state of the main system. The molecule is nonplanar in the upper triplet state also. The potential barrier is somewhat higher than for $^1A_2$.

Allison & Walsh (2) have analyzed the vibrational structure of a number of band systems of H_2CO and D_2CO in the vacuum ultraviolet (2000 to 1000 A). These band systems form Rydberg series. In the upper states of the first members of two of the Rydberg series, the molecule is nonplanar although the deviation from planarity is small.

Nonplanarity of a different type seems to apply to many of the excited states of C_2H_4 as already mentioned in last year's review [Wilkinson (205) and Wilkinson & Mulliken (207)]: viz., the two CH_2 groups are probably twisted against each other about the C—C axis.

Glyoxal, $(HCO)_2$, according to electron diffraction and infrared work, has a planar trans structure of point group C_{2h} in its ground state. The vibrational structure of the visible absorption of glyoxal in the region 4700 to 3700 A has been analyzed by Brand (19). King (85) has analyzed the rotational fine structure of the 0—0 band of both ordinary and deuterated glyoxal and has confirmed Brand's finding that the upper state is an A_u electronic state with the same molecular symmetry as the ground state (A_g). In both states the molecule is a nearly prolate symmetric top. Not all geometric parameters can be obtained but the sum $r(CC)+r(CO)$ changes from 2.726 to 2.742 A and the C—C—O angle from 121.9 to 125.0° in going from the ground to the excited state.

NO_2 has an extensive and complicated band system in the visible region. The great extent of this spectrum and the predominance of the bending frequency indicate a strong change of angle. Walsh (197) has suggested that the molecule is linear in the upper state. However, the evidence seems by no means conclusive. Robinson, McCarty & Keelty (169) have obtained the spectrum of NO_2 at liquid helium temperature in an argon matrix. The spectrum is surprisingly similar to that of the gas, which indicates that overlying hot bands are not the reason for the great complexity of the spectrum.

A new vibrational analysis of the 4800 to 2700 A absorption system of ClO_2 has been given by Coon & Ortiz (35). The molecule is bent in both the upper and lower states. The high intensities of bands corresponding to nonzero changes of the antisymmetric vibration can be accounted for only by the assumption that in the excited state the molecule is unsymmetrical, i.e., that the Cl—O distances are unequal.

Simple free radicals.—The spectra of an increasing number of free radicals have been observed and analyzed in the last few years. Again in several cases the equilibrium configuration is found to have different symmetry in the excited state from the ground state.

Dressler & Ramsay (48) and Ramsay (157) have made considerable progress in the analysis of the α bands of NH_2 and ND_2. They have shown that while the molecule is bent in the ground state it is linear in the excited

state of the α bands. For the upper state the effect predicted by Renner (165) of large anomalies due to the interaction of electronic and vibrational angular momenta has been clearly observed. It is probable that both the lower state and the upper state arise from a Π_u state of the linear configuration. The lower state forming one-half of the Π state has its potential minimum in a bent configuration (on account of a large Renner effect), while the upper state forming the other half of the Π state retains the linear equilibrium configuration. Possibly a similar situation applies in other molecules where a linear model would lead to a Π electronic state. The following geometrical data have been obtained for NH_2 in its ground state:

$$r_0(NH) = 1.025 \text{ A} \qquad \angle HNH = 103°20'$$

In the upper (linear) state the vibrational quanta increase rapidly with increasing v_2 rather than decrease in the normal way.

A situation similar to that in NH_2 seems to apply to PH_2 (and PD_2), that is, in all probability the molecule is bent in the ground state and linear in the first excited state [Ramsay (156)]; but a detailed analysis of the observed bands has not yet been made.

In HCO (and DCO) a progression of bands of simple structure (with P, Q, and R branch) have been found in absorption in the region 7500 to 4500 A [Ramsay (155) and Herzberg & Ramsay (66)]. The analysis shows unambiguously that in the lower state the molecule is bent (120°), and in the upper state it is linear. The CO distance in the ground state is 1.19_8 A; in the excited state 1.18_3 A.

The hydrocarbon flame bands which have long been ascribed to HCO do not belong to the same electronic transition as the absorption bands just discussed. If they are due to HCO they must involve at least one other electronic state of this molecule.

A further band system first observed under the same conditions as the regular DCO bands [Herzberg & Ramsay (66)] has now been shown to be due to the DNO molecule, and the corresponding HNO spectrum has also been found [Dalby (37)] in the region 7200 to 7600 A. Just as the NH_2 and HCO bands, the HNO bands are $\perp$ bands, but here the molecule is bent in both states involved. The angle changes from 109° in the lower state to 116° in the upper state, the $N-O$ distance from 1.212 to 1.241 A, and the $N-H$ distance from 1.063 to 1.036 A.

The CF_2 spectrum in the region 2400 to 3300 A observed in emission in a discharge tube was the first spectrum of a polyatomic free radical that was definitely identified [Venkateswarlu (192)]. It was also the first spectrum of a polyatomic free radical that was observed in absorption [Laird, Andrews & Barrow (94)]. A preliminary analysis [Venkateswarlu (192)] shows that the molecule is nonlinear in both states involved, but there is a considerable change of angle in going from the upper to the lower state. A more detailed fine structure analysis remains to be done.

The so-called **4050** group first observed in cometary spectra, later observed in discharges, in flames, in photolysis of various compounds, and in a carbon tube furnace, is now definitely identified as due to the C_3 radical [Douglas (44); Clusius & Douglas (33)]. The structure of the main band (at 4050 A) shows that the molecule is linear in both upper and lower state. The electronic transition is of the $\Sigma-\Pi$ or $\Pi-\Sigma$ type. The remainder of the spectrum is extremely complicated. Kiess & Broida (84) have recently analyzed a second band of similar structure at 4072 A, and in addition have given the wavelengths of a large number of lines and bands associated with the main bands and extending from 3600 to 4200 A. A vibrational analysis has not as yet been accomplished. The complications in the spectrum arise possibly from the Renner effect in the Π state. In addition to the discrete bands a continuum has been observed in the same spectral region by various investigators both in emission [Phillips and Brewer (147); Marr & Nicholls (112), and Kiess & Broida (84)] and absorption [Norrish, Porter & Thrush (139)]. It is probably of importance in N-type stars [McKellar & Richardson (116)].

A radical closely similar to C_3 is SiC_2. It was first identified by Kleman (86) in the spectrum of a carbon tube furnace charged with silicon. It consists of a number of bands in the region 4300 to 5650 A. The same spectrum had previously been observed in late N-type stars (Merrill-Sanford bands) but had remained unidentified for many years. In order to account for the vibrational structure of the spectrum it is necessary to assume that the molecule has the unsymmetrical form $Si-C-C$. A rotational analysis has not yet been accomplished and therefore it is uncertain whether or not the molecule is linear.

Thrush (187) has observed a new spectrum in the photolysis of HN_3 which in all probability is due to the free N_3 radical. The spectrum consists of a few somewhat irregularly spaced bands in a narrow region near 2700 A. No rotational or vibrational analysis has yet been made.

A spectrum of CH_3 was found by Herzberg & Shoosmith (67) in the flash photolysis of $Hg(CH_3)_2$ and several other compounds. It consists of a Rydberg series in the vacuum ultraviolet yielding an ionization potential of 9.840 ev, and a diffuse band at 2160 A. The corresponding spectrum of CD_3 has also been found. The analogue of the 2160 A band occurs at 2140 A and shows a simple, even though diffuse, fine structure. The interpretation of this fine structure leads to the conclusion that the CH_3 molecule is planar in at least one of the two states concerned, most probably in the upper state. It is probable that in the ground state the molecule is not planar but does not deviate much from a planar structure. This conclusion is however only tentative. Clouston & Cook (32) have described a spectrum near 3100 A which occurs in the flash photolysis of $Pb(CH_3)_4$ and $Pb(CD_3)_4$. It is not certain whether this spectrum is due to CH_3. It may be due to $Pb(CH_3)_x$ with $x = 1, 2,$ or 3.

The spectrum of the C_5H_5 radical was observed by Thrush (186) in the

flash photolysis of cyclopentadiene and ferrocene. It consists of line-like features at 29,581 and 29,911 cm.$^{-1}$.

Reviews of the spectra of free radicals have been given by Ramsay (158).

Molecular ions.—While a considerable number of spectra of diatomic molecular ions are known, only very few polyatomic molecular ions have been identified by their spectra. Until quite recently only one such spectrum, that of CO_2^+ was known [Bueso-Sanllehi (24) and Mrozowski (129)]. Three electronic states have been established: $^2\Pi_g$ (ground state), $^2\Pi_u$, and $^2\Sigma_u^+$, in all of which the molecule appears to be linear.

A few years ago Schüler & Reinebeck (175) observed an emission spectrum called by them "T spectrum" in the region 4800 to 6500 A in mild discharges through acetylene, benzene, and other organic compounds with He as carrier gas. This spectrum was recently studied under very high resolution and analyzed by Callomon (26). He showed that the T spectrum is due to the diacetylene ion $C_4H_2^+$. The transition is of the $^2\Pi - ^2\Pi$ type. The molecule is linear in both these states. On the basis of electron configurations a $^2\Pi - ^2\Pi$ transition involving the ground state is expected as a strong transition in the visible region. A fairly complete rotational and vibrational analysis has been made. The vibrational and rotational constants of the ground state are not very different from those of neutral C_4H_2.

Still more recently Callomon (27) has studied the spectrum of CS_2^+ first observed by Laird & Barrow (95) in discharges through CS_2 vapour. The assignment of this spectrum to CS_2^+, originally made on the basis of its similarity to that of CO_2^+, has been confirmed by Callomon's detailed fine structure analysis of one of the band systems near 2800 A, which turns out to be a $^2\Sigma_u^+ - ^2\Pi_g$ transition just as the 2900 A band system of CO_2^+. Like the CO_2^+ ion, the CS_2^+ ion is linear in both electronic states. The C—S distance in the ground state is 1.5542 A which may be compared to 1.5545 in neutral CS_2 [Stoicheff (181)].

More complicated molecules.—Four different electronic transitions have been recognized by Burnelle (25) in the visible and ultraviolet absorption spectrum of thiophosgene (Cl_2CS) and some excited state vibrational frequencies have been determined. The longest wavelength system is interpreted as a singlet-triplet system.

The ultraviolet absorption spectra of a number of benzene derivatives have been studied during the last two years: Rao & Sponer (160) have analyzed the near ultraviolet absorption spectrum of 1,2,4-trifluorobenzene. The 0—0 band is at 37,126 cm.$^{-1}$. Four vibrations in the excited state have been established. Matubara & Anno (113) have observed the absorption spectrum of 1,2,4,5-tetrachlorobenzene, assigning the band at 34,149 cm.$^{-1}$ as the 0—0 band. A tentative assignment of the vibrational frequencies in the upper and lower state has been made. Krishnamachari (93) has studied the near ultraviolet absorption spectra of ortho, meta, and para-fluorochlorobenzene finding the 0—0 bands at 37,035, 37,027, and 36,276 cm.$^{-1}$, respectively. A large number of bands have been found and analyzed in terms

of certain upper state vibrational frequencies and observed ground state Raman frequencies. Rao & Suryanarayana (161) have analyzed the near ultraviolet absorption spectrum of para-fluoroanisole ($F-C_6H_4-OCH_3$), obtaining for the 0—0 band 35,159 cm.$^{-1}$ and finding a number of vibrational frequencies in the upper and lower states. Suryanarayana et al. (183a) have studied the spectra of ortho-, meta-, and para-fluorotoluene as emitted in fluorescence and in an ozonizer type of discharge and have compared them with the absorption spectra. The spectra of p-dimethoxy-benzene and m-bromotoluene have been studied by Sen (177). He finds the 0—0 bands to be at 33,843 and 36,526 cm.$^{-1}$, respectively. Robertson, Babb & Matsen (166) have investigated the effect of high pressures (up to 550 atm. of N_2) on the near ultraviolet absorption spectra of benzene, toluene, fluoro- and chloro-benzene, and phenol. The spectra were found to broaden asymmetrically and to shift to longer wavelengths. The emission spectrum of C_6H_5Cl has been obtained by Schüler & Lutz (173).

A system of extremely sharp absorption bands in the region 2900 to 3300 A, originally found by Reid (164) and ascribed to a triplet←singlet transition in the pyridine molecule, has been shown by Brealey (22) to be due to pyrazine; it has recently been analyzed in detail by Ito et al. (76). They have found that these bands belong to two electronic transitions, one having sharp and the other somewhat broader bands. The first one is an allowed transition with its 0—0 band at 30,875 cm.$^{-1}$; the second one is a forbidden transition with the 0—0 band missing. The spectrum of pyridine 1-oxide in the near ultraviolet has been observed and analyzed by Ito & Mizushima (75). The 0—0 band is at 29,299 cm.$^{-1}$. Vibrational frequencies in the upper and lower states have been established. The spectrum of 2:5-dimethyl furan was studied by Santhamma (170) who found the 0—0 band at 40,541 cm.$^{-1}$ and established six excited state vibrational frequencies.

DISSOCIATION, PREDISSOCIATION, AND IONIZATION

While many continuous absorption spectra are observed in various polyatomic molecules, their interpretation in terms of specific dissociation processes presents considerable difficulties. Only in a few cases have definite conclusions been drawn as, e.g., in the continua of the methyl halides which clearly correspond to dissociation into CH_3+X, or the first absorption continua of H_2O and H_2S, which in all probability correspond to photodissociation into $OH+H$ and $HS+H$, respectively. Only upper limits have as yet been obtained from these continua for the corresponding dissociation energies.

Many absorption band systems of polyatomic molecules consist of diffuse rather than sharp bands, and in many instances the diffuseness is not due to insufficient resolution but to predissociation, i.e., the possibility of a radiation-less transition to a continuous range of energy levels. In the first absorption system of HCN (the $\alpha \leftarrow X$ bands) the phenomenon of predissociation appears in a very striking manner [Herzberg & Innes (65)]. In each

progression at a certain v' value the individual lines in a band begin to be slightly diffuse. With increasing v' this diffuseness becomes more pronounced until the whole band is just one narrow continuum. The beginning of the diffuseness starts at different energies for different vibrations. For DCN it starts in each progression at a somewhat higher energy than for HCN, presumably because D can less easily penetrate a potential hill than H. For a given vibrational level in the upper (α) state, in which the molecule is nonlinear, the diffuseness (i.e., the predissociation probability) increases markedly with increasing rotational quantum number K. In the much stronger γ—X system of HCN the bands are diffuse from the start but again the diffuseness increases in each progression.

Another striking predissociation occurs in HCO and DCO [Herzberg & Ramsay (66)]. Here, under high resolution, alternate bands in the main progression appear to be missing but at low resolution it is found that these alternate bands occur as diffuse bands. Since the molecule is linear in the upper state (unlike the lower), alternate bands have even and odd l values (or $K = |l+\Lambda|$ values). The sharp bands correspond to $l=0$. The bands in between them have, therefore, $l=1, 3, \ldots$. The diffuseness of the bands with $l>0$ is presumably due to a reason similar to that of the increase of diffuseness with K in HCN. A detailed explanation of this effect has not yet been given.

A very strong isotopic effect of predissociation is found for the methyl radical [Herzberg and Shoosmith (67)]. CH_3 shows a diffuse band without structure except for two intensity maxima. CD_3 shows a clearly resolved fine structure even though it is still somewhat diffuse.

The predissociation in H_2CO has been further studied by Brand & Reed (21). They suggest the existence of a second weak predissociation in addition to the well-known strong one starting at 2850 A. This weak predissociation is revealed by the breaking off of the emission spectrum for all but the levels with $v_4' = 0$. (This appears to be the first case of breaking off on account of predissociation established in a polyatomic molecule.) This predissociation leads to an upper limit of 28,740 cm.$^{-1}$ for the dissociation energy of H_2CO into $H+HCO$, a value that is close to the value 75.1 kcal./mole resulting from electron-impact experiments.

Ionization continua always join on to Rydberg series; the series limits represent accurate values of ionization potentials. The limit may be established by measuring the actual production of ions or by determining the limit of the Rydberg series. Both methods have been applied again to a number of cases. Watanabe & Mottl (201) have redetermined the ionization potential of NH_3 by the first method obtaining 10.15_4 ev, slightly correcting the earlier value 10.07 of Walker & Weissler (194). The former authors have resolved the ionization potentials corresponding to the different vibrational levels of NH_3^+. The strong excitation of the bending vibration in the ion (as well as in the higher members of the Rydberg series) corresponds to the fact that NH_3^+ (like CH_3) is planar or nearly planar while NH_3 is not. Watanabe

and Mottl have also obtained the ionization potentials of CH_3NH_2 and other amines; these turn out to be appreciably smaller than that of NH_3. Watanabe (199) has determined the ionization potentials of a large number of polyatomic molecules by the photoionization method. In most cases the values obtained agree very satisfactorily with those obtained from Rydberg series. As an example the case of C_6H_6 (and C_6D_6) may be cited. Here, following earlier work of Price & Wood (152), Wilkinson (203) has recently measured and analyzed a number of beautiful Rydberg series which yield $I.P.$ $(C_6H_6) = 9.247$ ev and $I.P. (C_6D_6) = 9.251$ ev, while Watanabe finds 9.245 ev by the photoionization method.

The Rydberg series found for CH_3 and CD_3 (67) yield ionization potentials of 9.840 and 9.832 ev, respectively. Contrary to the usual situation here the ionization potential of the deuterated molecule is smaller than that of the ordinary molecule, indicating a greater difference of zero-point energy in the ionized than in the neutral molecule.

THEORETICAL WORK

The recent work on the rotational fine structure of the electronic spectra of polyatomic molecules has shown the need for a better theoretical understanding of the finer interactions of rotation, vibration, and electronic motion. In some cases these interactions give rise to rather large effects and make an analysis very difficult.

According to early work of Jahn & Teller (78) the interaction of vibration and electronic motion causes degenerate electronic states of nonlinear polyatomic molecules to split such that two states result whose potential minima lie on opposite sides of the symmetrical configuration.

A more quantitative study of the variation of the electronic energy with distortion of the originally symmetrical molecule has been made, particularly for XY_6 molecules of octahedral symmetry by Öpik & Pryce (144). The way in which the Jahn-Teller effect affects the vibrational levels of the degenerate electronic states has been investigated in detail by Longuet-Higgins et al. (109a) [see also Moffitt & Liehr (120a) and Moffitt & Thorson (120b)]. In addition, the effect on the selection rules and the intensity distribution in a transition between such a degenerate state and a nondegenerate state have been discussed.

From an experimental point of view the Jahn-Teller effect in some of the Rydberg levels of C_6H_6 has been discussed by Wilkinson (203). An anomalously high intensity of transitions involving the ν_{18} (e_{2g}) vibration is explained by a Jahn-Teller distortion of the molecule in the excited states into a configuration of D_{2h} symmetry. Calculations on this Jahn-Teller distortion have been made by Liehr & Moffitt (104) who conclude that $\Delta v = 1, 3, \ldots$ are allowed for ν_{18} as well as $\Delta v = 0, 2, 4 \ldots$ and that therefore, contrary to Wilkinson's conclusion, the observed interval (695 cm.$^{-1}$) gives directly ν_{18} in the excited state (not $2\nu_{18}$). It may be compared with 606 cm.$^{-1}$ in the ground state.

The importance of the Renner effect for an understanding of the electronic spectra of linear molecules has recently been emphasized by Dressler & Ramsay (48).

At the recent Ottawa symposium on the structure (and reactivity) of electronically excited species, Linnett (105) has used the concept of equivalent orbitals introduced by Lennard-Jones for an attempt of understanding the reasons for the change of molecular configuration in going from the ground state to the first excited state of C_2H_2, HCO, and NH_2. At the same symposium Mulliken (126) has discussed the same question on the basis of recent molecular orbital calculations using as examples the molecules C_2H_2, HCN, CO_2, CS_2, O_3, and generally AB_2. While it is possible to gain an understanding of the changes of configurations upon excitation, there is still no certain method of unambiguous prediction of this behaviour. It must, however, be recorded that Walsh (196) in his early work, without knowledge of the later results, was remarkably successful in his predictions.

The electronic structures of a number of molecules have been discussed during the past year, mostly on the basis of molecular orbital theory, even though this period has not been one of very great activity in this field. A very detailed and extensive discussion of the electronic structure of ozone has been given by Fischer-Hjalmars (51) who has computed the dissociation energy and the dipole moment of the ground state, as well as the transitions to the lowest excited states, and compared the results with the available experimental data.

A molecular orbital treatment of diborane, considering only the two B atoms with the two bridge H atoms, that is considering it as a four-center, four-electron problem, has been given by Hamilton (56). A more complete treatment considering diborane as a twelve-electron system has recently been given by Yamazaki (214).

While in these papers the usual linear combinations of atomic orbitals are used for the molecular orbitals, Carter (29) and Koide, Sekiyama & Nagashima (91) have used instead, in the case of highly symmetrical molecules like CH_4 and SiH_4, expansions in terms of spherical harmonics about the central nucleus as origin and have obtained satisfactory values for energies, bond lengths, and force constants, using only the first term in each expansion.

Hurley (71) has further developed an electrostatic interpretation of chemical binding using optimum paired-electron orbitals. On this basis the properties of covalent bonds can be understood entirely in terms of Coulomb forces between atoms.

A good deal of molecular orbital work has been done on more complicated systems. We mention only the work of McWeeny (117) and McWeeny & Peacock (118) on heterocyclic systems. They have used self-consistent molecular orbitals with limited configuration interaction for the discussion of the ground states and low excited states of pyridine, pyrazine, and similar systems. [See also Pritchard & Sumner (153).]

In the theoretical study of the low excited states of benzene and its derivatives, normally only singly excited states are considered, that is, states in which only one electron is in an orbital higher than those occupied in the ground state. Murrell & McEwin (127) have obtained an improved agreement with observation by introducing doubly excited states and their effects on the singly excited states. The general question of the validity of the π-electron approximation, almost always used for benzene and its derivatives, has been discussed by Lykos & Parr (110) and the conditions under which it can be applied have been established. The contribution of d-orbitals to chemical binding has been discussed by Craig & Magnusson (36a).

In highly symmetric molecules many electronic transitions are forbidden by selection rules. However, for polyatomic molecules, unlike diatomic molecules, during certain vibrations the symmetry of the molecule is lower in the displaced position than in the equilibrium position, and therefore the interaction of vibration and electronic motion makes possible the occurrence of symmetry-forbidden transitions [Herzberg & Teller (68)]. The C_6H_6 bands near 2600 A are well-known examples of such symmetry-forbidding transitions. Murrell & Pople (128) have calculated the intensities of these transitions as well as of the 1800 A system of C_6H_6 using the molecular orbital method. Pople & Sidman (149) have carried out similar calculations for the near ultraviolet bands of formaldehyde (H_2CO) which, if the molecule were planar in both upper and lower state, would represent a forbidden transition.

Goodman, Ross & Shull (55) have calculated on the basis of molecular orbital theory the intensities of the near ultraviolet absorptions in substituted benzenes (C_6H_5X) for which, on account of the lower symmetry, the transitions are no longer symmetry-forbidden. Longuet-Higgins & McEwen (109) have made calculations of the ground and excited states of the cyclic radicals and ions C_3H_3, $C_3H_3^+$, $C_4H_4^{++}$, $C_4H_4^{--}$, C_5H_5, $C_5H_5^-$, C_7H_7, $C_7H_7^+$, $C_8H_8^{++}$, $C_8H_8^{--}$ by a semi-empirical molecular orbital method. Calculations of the probabilities of triplet-singlet transitions in benzene and in ketones have been made by Hameka (55a).

A review of the molecular-orbital and equivalent-orbital approach to the electronic structure of molecules has been given by Pople (148). A good deal of theoretical work has been carried out on more complicated molecules, particularly polycyclic molecules; but this will not be reviewed here.

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SPECTROSCOPY[1,2]

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The general high level of activity in all areas of molecular spectroscopy has been maintained during the past year. Therefore the present review is not exhaustive, but contains material which was of particular interest to the reviewers. It is indicative of the interest shown in all phases of molecular spectroscopy that a new journal, *Journal of Molecular Spectroscopy*, has appeared and the journal *Spectrochimica Acta* now emphasizes nonanalytical spectroscopic contributions.

ROTATION SPECTRA

Compared to the early years of microwave spectroscopy, relatively few papers reporting such investigations were published in 1957. Most of the papers which did appear dealt primarily with the complexities of the spectra. Some of the molecules investigated along with the parameters obtained are outlined below (Table I).

Perhaps the most important and exciting problem today in molecular structure is that of the origin of the barrier to rotation about single bonds. The analysis of rotational spectra provides a powerful tool for the elucidation of this question. One method depends on the intensity difference between identical rotational transitions originating in different torsional states. It is possible to observe these transitions, for the moments of inertia of the molecule will be different in excited vibrational states from those in the ground state with a resulting difference in the frequency of the rotational transitions. The relative intensities with which these transitions occur are to a good approximation proportional to the population of the states. Consequently, the measurement of the relative intensities of lines corresponding to the same rotational transition in different vibrational states can lead to a determination of the energy difference between the states. In this way Dailey and his collaborators have continued their study of hindered rotation in substituted ethanes by examining ethyl bromide (1) and ethyl chloride (2). They have applied the same technique to formic acid (3) and propionitrile (4). The practical difficulties of this method at the present time are considerable and reside in large measure in the difficulty of making accurate relative intensity measurements. This difficulty increases as the frequency separation of the lines increases. Consequently barriers to internal rotation obtained by this method may not be precise.

Recently Wilson and his co-workers (5) have developed a much more ac-

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[1] The survey of literature pertaining to this review was concluded in mid-January, 1958.

[2] Contribution No. 251 from the Department of Chemistry, Tufts University.

curate procedure for studying internal rotation and obtaining the height of the hindering barrier. If the barrier is very high, the torsional oscillations of the CH_3 group in a molecule like CH_3CHO are small and confined to three separate potential wells. As the barrier becomes lower, tunneling between the wells occurs which results in each triply degenerate torsional level, v, being split into a nondegenerate level, v_A, and a doubly degenerate level, v_E. Molecules in these two levels have somewhat different rotational transition energies and lead to the occurrence of doublets with a barrier-dependent separation. As this experimental method depends upon the measurement of a frequency difference, it can lead to very precise computation of the barrier height. This method has been applied to CH_3CHO (5), CH_3BF_2 (6), methyl silane (7), acetic acid (8), and *trans*-fluoropropylene (9). Wilson has published a summary of these and other experimental results (10). Herschbach (11) has investigated the effect of higher than second-order terms on the coupling between internal and over-all rotation. He has shown that third and fourth-order terms account for certain small discrepancies in the second-order treatment of some of the above molecules and that the V_6 correction introduced in acetaldehyde (5) and methylsilane (7) is spurious. Lide & Mann have analyzed similar data by the method of Hecht & Dennison (12) to obtain barriers for propylene (13) and methylallene (14). Hecht & Dennison (15) have applied their formulation of the theory of hindered rotation with excellent results to the $J = 0 \rightarrow 1$, $K = 0 \rightarrow 0$ transition of CH_3OH. They were able to predict the 30 observed separations with only six empirical constants.

Since the splitting of the rotational lines decreases as the height of the barrier increases, the method is limited to molecules with barriers less than about 1800 cal./mole. However, whatever the barrier height, there should be rotational transitions of sufficiently high rotational quantum number to exhibit splitting. Unfortunately these are frequently inaccessible experimentally or cannot be identified. An alternative procedure is to examine the rotational spectrum of excited torsional states where the effective barrier is smaller and the splitting correspondingly greater. This method has been used by Swalen & Herschbach to analyze the microwave spectrum of propylene oxide (16). Here the splitting in the first excited torsional state is about 50 times greater than it is in the ground state. Although the barrier heights obtained by analysis of the ground state and first excited state differ slightly, it has been shown that this is due to the inadequacy of the second-order perturbation treatment (11).

The study of methylamine is further complicated by the inversion of the NH_2 group in addition to internal rotation. Lide has analyzed the spectrum of CD_3ND_2 (17) by a procedure justified by Kivelson & Lide (18), who treated the case where the barriers to inversion and rotation are high.

A complete structural determination has been reported on the important formamide molecule by Kurland & Wilson (19). It was demonstrated that the molecule in the gas phase is planar and that the dipole moment is di-

TABLE I

STRUCTURAL INFORMATION FROM MICROWAVE SPECTROSCOPY

Molecule	Bond	Length (A)	Angle	Dipole Moment (Debye)	Torsional Frequency (cm.⁻¹)	Barrier Height (cal./mole)	Reference
CH_3CHO CD_3CDO CD_3CHO	Methyl group CH CD CC Aldehyde CH CO	Methyl group 1.088 1.086 1.501 Aldehyde 1.114 1.216	Methyl group HCH 108°16' DCD 108°32' Aldehyde CCH 117°29' CCO 123°55'	2.69		1162±30 1151±30 1143±30	(5)
NH_2CHO	CO CN NH	1.243 ±0.007 1.343 ±0.007 0.995 ±0.007	HNH 118.98±0.50° NCO 123.58±0.35° NCH 103.9±1.2°	$3.71_4 ±0.06$		Also gives quadrupole coupling constants	(19)
$CF_2=CH_2$ $CF_2=CHD$	CF CC	1.321 ±0.005 1.311 ±0.005	FCF 109°15'±25' Assumed HCH = DCD = 120°	Makes an angle of 39.6° with CN bond			(25)
$CF_2=CD_2$	CD	1.10 ±0.05					(24)
CF_3CH_3 CF_3CH_2D CF_2CD_2H CF_2CD_3	CC CF CH} CD}	1.530 ±0.005 1.335 ±0.005 1.085 ±0.008	CCF 111°02'±17' CCH 108°19'±35'				
C_2H_5Br	CC CH CBr	1.5495 1.110 1.9400	CCH 110°00' CCBr 110°30'		202	2800	(1)
C_2H_5Cl	CC CH CD CCl	1.5495 1.101 1.090 1.7785	HCH 110°00' CCCl 110°30'	Staggered configuration	Estimated at 236 cm.⁻¹	3400	(2)

TABLE I (continued)

Molecule	Bond	Length (Å)	Angle	Dipole Moment (Debye)	Torsional Frequency (cm.⁻¹)	Barrier Height (cal./mole)	Reference
SiH₂F₂	SiF	1.471 ±0.007	FSiF 107°56'±6'				(23)
	SiH	1.5767±0.001	HSiH 112°1'±30'				
SiD₂F₂	SiD	1.469 ±0.010	FSiF 107°57'±10'				
	SiF	1.5764±0.001	DSiD 113°11'±45'				
CH₃BF₂				1.67±0.02		13.77±0.03	(6)
SO₂F₂	SO	1.405 ±0.003	OSO 123°58'±12'	1.110±0.015			(27)
	SF	1.530 ±0.003	FSF 96°7'±10'				
s-*trans* acraldehyde				3.11±0.04 oriented 14° from the CO group	200±50	lower limit ≈2300	(26)
CF₃C≡C—CH₃	CF	1.340	FCF 106°08'				(22)
CF₃C≡C—CD₃	C—C	1.455	HCH 108°30'				
	C≡C	1.189					
	CH	1.097					
Propylene oxide						2710 from ground state 2560 from first excited state	(16)
CH₃SiH₃	SiC	1.8668 ±0.0005	HSiH 108°15'±30'	Staggered configuration	1700±100		(7)
	SiH	1.485 ±0.005	HCH 107°40'±30'				
	CH	1.093 ±0.005					
BrF₃	BrF	1.721	FBF 86°12.6'				(20)
	BrF	1.810					
HCOOH	CH	1.085	OCO 124°18'		~667±41	1700	(3)
	C=O	1.245	COH 107°48'				
	C—O	1.312					
	OH	0.95					

Molecule	Bond	Length (Å)	Angle	Dipole Moment (Debye)	Torsional Frequency (cm.⁻¹)	Barrier Height (cal./mole)	Reference
C_2H_5CN	CC (ethyl)	1.5479	CCC 110°32'		~226	3280 ± 290	(4)
	CC (nitrile)	1.4735	HCH 109°19'				
	C≡N	1.1566					
	CH	1.0914					
CD_3ND_2	CN	1.474	DND 105°52'	1.326 ± 0.015		Also gives quadrupole coupling constants 1956 ± 6	(17)
	ND	1.011	CND 112°3'				
OCS				0.7124 ± 0.0002			(29)
trans-$CH_3CH{=}CHF$						2200 ± 100	(9)
$CH_3CH{=}CH_2$	C—C	1.488	CCC 124°45'	0.364		1978 ± 17	(13)
	C=C	1.353					
$CH_3CH{=}C{=}CH_2$				0.401		1589 ± 6	(14)
CH_3COOH	C—C	1.497 ± 0.010	CCO 119°30' ± 30'				(8)
	H toH in Me group	1.733 ± 0.025	HCH 106°48' ± 4°				
CH_3NH_2	CN	1.474	CNH 112°10'	$\mu_\|$ 0.304		1975	(33)
			HNH 105°50'	$\mu_\perp$ 1.232			
			HCH 109°30'				
CH_3SH	SH	1.336 ± 0.01	CSH 96°30' ± 1°	$\mu_\|$ 1.35 ± 0.05		1269 ± 28	(34)
	CS	1.819 ± 0.005	HCH 109°45' ± 30'	$\mu_\perp$ 0.64 ± 0.05			
	CH	1.091 ± 0.01					
$CH_2{=}CCl_2$	CCl	1.727	ClCC 123°10'				(35)
TlI	TlI	2.8136 ± 0.003					(36)

rected at an angle of 39.6° from the CN bond. Magnuson has shown BrF$_3$ to have a planar, distorted "T" structure (20). Other determinations of structure include fluorobenzene (21), trifluorobutyne (22), difluorosilane (23), 1,1,1-trifluoroethane (24), CF$_2$=CH$_2$ (25), acrolein (26), and SO$_2$F$_2$ (27). In the latter molecule the S—O distance has been found to be 1.405 A, which replaces the anomalously short bond length reported previously (28).

Using an improved microwave spectrograph permitting measurements of electric field intensities to one part in 10,000, Marshall & Weber (29) determined the dipole moment of OCS to be 0.7124 ± 0.0002 D. Effects caused by the fourth-order term in the perturbation expansion of the Stark effect were observed and found to be in good agreement with theory. Gordy and co-workers (30, 31) measured the rotational transitions of symmetric top molecules in the 1 to 4 mm. region. Rosenblum & Nethercot (32) find the quadrupole coupling constant for CO^{17} to be four times larger and of opposite sign than that reported for OCS, where a similar bond structure might be expected. The derived value of eqQ for CO^{17} is at variance with valence bond and molecular orbital calculations for this simple molecule.

Interest in far infrared spectra has increased in the past few years, as evidenced by the construction of several large instruments designed specifically for this region of the spectrum (37, 38, 39). This year increased impetus has been given to investigations in this spectral region by the successful conversion of a small commercial spectrometer by Lord & McCubbin (40). They report resolution of about 0.3 cm.$^{-1}$ from 5 to 50 microns and 0.5 to 1.0 cm.$^{-1}$ beyond 50 microns.

Palik & Oetjen (41) studied H$_2$Se and found $r_{H-Se} = 1.46$ A and $\angle$HSeH $= 91.0°$ while Palik & Rao (42) reported on the methyl halides. The inversion splitting of NH$_2$D lines in the far infrared has been observed and the effect of centrifugal distortion on the energy levels discussed (43). Stoicheff has continued his high resolution studies of pure rotational transitions in the Raman effect. The C—H bond distance in diacetylene is reported to be shorter than that in acetylene, and in dimethylacetylene at least one of the C—C bonds is longer than that observed in methylacetylene (44). A complete set of constants for the $v=0$ and 1 levels of H$_2$, HD, and D$_2$ have been determined (45). From the rotational spectrum of butatriene (46), it was deduced that the central C=C bond is shorter than in ethylene and allene. However, this result is based on the assumption that the two outer bonds in butatriene are of the same length as the C—C bonds in allene.

VIBRATION SPECTRA

The increased availability of high-quality gratings and detectors has greatly expanded activity in high resolution infrared spectroscopy. Although the well-known centers of high resolution work still dominate the literature, other laboratories are getting into operation. The work of Lord & McCubbin with modified, small commercial instruments (47) has accelerated this trend.

Rank and co-workers have continued their very high resolution studies

in the near infrared and have studied l-type doubling in three π-π bands of HCN (48). Further measurements on HCN coupled with the B value obtained from microwave spectra yield a value of 299793.2 ± 1.8 km./sec. for the velocity of light (49). Dixon & Sheppard (50) have given a complete assignment for silyl iodide. An analysis of the rotational fine structure with an assumed value for the Si—H bond distance yielded an Si—I distance of 2.435 ± 0.001 A and an H-Si-H angle of $109° 54' \pm 24'$. Rao, Nielsen, & Fletcher (51) have analyzed four type E fundamental bands of allene and concluded that $r_{C-H} = 1.069$ A and $\sphericalangle \text{HCH} = 116.9°$. Shuler & Fletcher (52) made a complete assignment of fundamentals for 1,1-dideuteroallene while Rao & Palik (53) looked at some type E bands of allene, allene-d_4, methylacetylene, and methyl cyanide. Molecular constants were reported for OCS (54). The ν_3 band of methane has been studied by Allen & Plyler (55). Gray & Lord (56) obtained some rotational constants from a study of methylamine and its deuterium derivatives. The first overtone of the torsional mode occurs at a frequency consistent with a barrier height of 690 cm.$^{-1}$. A grating study of TF yielded $\omega_e = 2508.5$, $\omega_e x_e = 32.5$, and $r = 0.97$ A (57). Jones has studied DI under medium resolution (58), and all six fundamentals of formaldehyde have been subjected to grating resolution by Willsen & Blau (59). Another investigation of the fundamental band of $N^{15}O$ has been reported (60). The molecular constants of NH_3 and ND_3 obtained from high resolution studies of a number of fundamental, overtone, and combination bands have been summarized by Benedict & Plyler (61). Courtoy (62) has studied CO_2 in the near infrared under high resolution. H_2S (63) and CH_3CN (64) have also been investigated with grating resolution. The infrared (65, 66) and Raman (67, 68) spectra of various deuterated and boron isotopically substituted species of borine carbonyl have been observed and approximate normal coordinate treatments made. Bethke & Wilson (69) have reported the infrared and Raman spectra of Si_2H_6 and Si_2D_6. Donovan (70) has continued his interesting work on the spectra of cool flames.

The calculation of rotational energy levels for asymmetric top molecules is always troublesome. Polo (71) has eased this situation somewhat by deriving expressions for the power series coefficients which give the explicit dependence of these coefficients on J, K, and an asymmetry parameter ϵ. First order corrections for centrifugal distortion in terms of J, K, and ϵ also have been included. Other theoretical papers include an operational derivation of symmetric rotor wave functions by Shaffer (72), a start on the much-needed calculation of band contours by Edgell & Moynihan (73), and the consideration of rotational distortions in linear molecules by Amat & Nielsen (74). Nielsen et al. (75, 76) have continued their work on higher-order rotation-vibration energies of polyatomic molecules. Poltorak (77) has predicted CH_3 to be pyramidal, CH_2 to be nonlinear, and $B_3N_3H_6$ to have two structural isomers.

Nielsen and his co-workers have pursued their study of fluorinated com-

pounds (78, 79, 80, 81) and fundamentals also have been assigned in CCl_3CN (82), s-trioxan (83), N-methylformamide (84), PCl_5 (85), and $VOCl_3$ (86). A tentative assignment of bands has been made for dimethylphosphine (87). Other molecules reported include ketene and deuteroketene (88), methyl borate (89), cyanoacetylene (90), halogenated methyl cyanides (91), trans-dichlorodifluoroethylene (92), tetramethylhydrazine (93), and diphosphine (94, 95).

In the gaseous and liquid states the trans and gauche forms of ethyl methyl sulfide (96) and normal alkyl bromides (97) have nearly the same energy. Mizushima and his collaborators in their continuing investigation of internal rotation have shown that in 1,2-dichloro-2-methyl propane (98) the energy difference in the gaseous state between the trans and gauche forms is about 1 kcal./mole. This difference almost disappears in the liquid state. Ketelaar & van Meurs (99) have computed the energy difference between rotational isomers of some dipolar molecules in the liquid state from the observed dipole moments. Mann & Fano (100) estimated the barrier to rotation about the B—B bond in B_2Cl_4 to be 1700 ± 600 cal./mole. Assignments have been made for 1-chloro-2-bromoethane (101), disulfur decafluoride (102), CH_3D, CH_2D_2, and CD_3H (103), toluene and m-xylene (104), $HC(CD_3)_3$ and $DC(CH_3)_3$ (105), and pyridine (106).

The H_3O^+ ion previously has been identified by nuclear magnetic resonance spectra in crystalline hydrates of strong acids and by its vibrational frequencies in the solid state. Falk & Giguere (107) have now succeeded in determining the spectrum of the hydronium ion in liquid solutions. They measured the absorption spectrum from 2 to 25 microns of aqueous solutions of HCl, HBr, HNO_3, $HClO_4$, H_2SO_4, H_3PO_4, and some salts in various concentrations at room temperature. In all cases broad bands were found near 1205, 1750, and 2900 cm.$^{-1}$ arising from the H_3O^+ ion. These are in good agreement with the frequencies observed in the crystalline acid hydrates. The intensities of the bands were approximately proportional to the "hydrogen ion" concentration and cooling or even supercooling produced no significant changes in the spectra. Klemperer and his co-workers have continued their interesting infrared measurements at high temperature. Reports were published on alkali halides (108, 109) and CuCl (110).

Woodward & Anderson (111) studied the Raman spectra of tin (IV) bromide containing varying concentrations of HBr. At high concentrations of HBr a new spectrum was obtained which, according to the number of lines and their depolarization factors, is that expected for an octahedral species. In attributing this spectrum to $SnBr_6^=$ they suggest that the conclusion of previous workers that this ion has lower than octahedral symmetry was due to the assignment of all the lines observed in the mixture to $SnBr_6^=$ when the solution must have contained other species. Woodward et al. have also investigated S_2F_{10} and Te_2F_{10} and interpreted the spectra on the basis of the staggered D_{4d} configuration (112, 113). Raman data have been published for triethyl borane (114), gaseous trifluoroacetonitrile (115), and gaseous dimethyl ether (116).

Some optically inactive amino acids have been studied and the functional group frequencies correlated with structure (117). The spectra indicate that betaine hydrate is a dipolar ion in the form of a water complex. The Raman spectrum of cyclobutene is characterized by the absence of many vibrational frequencies permitted by the selection rules to occur in the Raman effect. The carbon-carbon double bond vibration occurs at the unusually low frequency of 1566 cm.$^{-1}$ (118, 119). Trifluoroacetic acid exists in both monomeric and dimeric forms in the gas phase at room temperature, but at 100° the vapor is predominantly monomeric. From the temperature dependence of the OH stretching frequencies, Kagarise (120) has determined the heat of dissociation in the dimer-monomer reaction to be 13.7 ± 0.4 kcal./mole. From spectroscopic studies of hydrogen bonding in methyl, ethyl, and tertiary butyl alcohol, Liddel & Becker (121) have deduced that the enthalpies of dimer formation are respectively 9.2 ± 2.5, 7.2 ± 1.6, and 4.8 ± 1.1 kcal. per mole of dimer. These high values were interpreted to mean that the dimer is cyclic with two non-linear hydrogen bonds.

Interest continued strong in the determination of potential-energy functions for molecular systems. However, in only a few cases were sufficient data available to permit the use of a most general potential-energy expression. This situation is particularly unfortunate in view of the great need for accurate potential constants and normal coordinates in both intensity calculations and barrier problems. Although meaningful analyses of this type demand a great deal of experimental work and often are tedious, the results can be very rewarding. Crawford *et al.* (122) carried out a normal coordinate analysis of the methyl halides. The potential-energy functions found by Chang (123) were put into the more useful valence-type form and revised to accord with the true nontetrahedral geometry. The normal frequencies were corrected for Fermi resonance and anharmonicity. The fit was extended from the normal frequencies to include the Coriolis coupling constants and centrifugal distortion coefficients. By using a combination of a simple valence force field and a Urey-Bradley field and the transfer of force constants, Mann *et al.* (124, 125) have analyzed the fundamental vibrations of 27 perhalogenated ethylenes. Weston (126), from an investigation of $N^{15}O_2$, has been able to calculate all four potential constants for nitrogen dioxide. Less complete analyses have been made on cyclopentane (127), neopentane (128), $M(XY)_6$ molecules (129), $M(XY)_4$ molecules (130), HNO_2 (131), *cis* and *trans* 1, 2-dibromoethylene (132), and $Fe(CO)_5$ (133). This latter investigation infers that the Fe—C bonds in $Fe(CO)_5$ are stronger than the Ni—C bonds in $Ni(CO)_4$. Wilson (134) has given explicit expressions relating the centrifugal distortion coefficients of symmetric top molecules to the vibrational force constants.

INTENSITIES

The determination of the absolute intensity of vibration-rotation bands in the infrared spectrum or the Raman effect is attractive, as these measurements should lead to an increased understanding of molecular electronic

structure. Unfortunately, at the present time these investigations are hindered by both experimental and theoretical difficulties. The measurement of infrared intensities by the Wilson-Wells technique (135) is plagued by problems of resolving power, the overlapping of bands, and the frequent occurrence of strong Coriolis coupling between vibrations. The first of these can be minimized by using sufficient pressure-broadening and the requisite spectrometer, while the second yields to a comparison of the results from several isotopic species. In this way Crawford and his co-workers have continued their very careful measurements and have reported on C_2H_6 and C_2D_6 (136) as well as methyl and trideuteromethyl chloride, bromide, and iodide (137). The rate of change of dipole moment with respect to symmetry coordinates during the vibration was computed and interpreted in terms of effective bond moments. That is, the dipole moment changes are regarded as due to small effective moments and charges attached to the bonds of the molecule. This attractive interpretation is not without its difficulties for it is realized that bond dipole moments and their derivatives depend not only on the bond primarily involved, but also on the molecule and symmetry of the vibration from which they are determined. Indeed, Coulson & Stephen (138) have again stressed the limitations of any theory in which the total molecular dipole moment is divided into components of fixed magnitude associated with particular bonds. They computed the intensities of some vibrations of C_2H_2, C_2H_4, and C_6H_6, and demonstrated for these molecules the failure of the fixed-bond moment hypothesis. By the inclusion of the appropriate amount of bond following and change in hydridization an approximate fit with experimental results was obtained. It is not clear at this point whether the inclusion of these additional effects which cannot be independently determined is a significant improvement over the bond moment hypothesis.

The intensities and bond moments in SO_2 have been studied by Mayhood (139). As might have been expected, the amount of charge redistributed in the distortions of the molecule was found to be much greater than the formal charges at equilibrium. Again the discussion of the observed intensities of SO_2, as that of NH_3 and HCN, included an estimation of the contribution of unshared pairs, re-hybridization, and orbital following. To the contrary, for the stretching motion in $CO^{16}O^{18}$, Eggers & Arends (140) find the oscillating dipole moment of the molecule to be well represented by two independent oscillating bond moments.

The "curve of growth" method (141) which suffers less from experimental difficulties than does the Wilson-Wells technique has been used to determine the absolute intensity of the 721 cm.$^{-1}$ and 742 cm.$^{-1}$ bands of CO_2 (142). The 667 cm.$^{-1}$ band of CO_2 has previously been investigated with the same technique by Kaplan & Eggers (143). Although the experimental difficulties are less with this method, a great deal must be known about the molecule for the method to be applied. Hence, it is doubtful whether this technique will have general usefulness. Benedict et al. have continued their work on

individual line strengths in diatomic molecules to report on HCl and DCl (144). Woodward and co-workers (145) have reported on some Group IV tetrahalides as part of their continuing work on Raman intensities.

Much interest continues in the intensity of absorption bands in condensed phases. Russell & Thompson (146) examined the influence of spectrometer slit width upon the shapes of vibrational bands in some pure liquids and solutions. They also considered the relative significance of extinction coefficients and integrated band intensities for quantitative work. Brown (147) has considered solvent effects in solution. A study of the cyanide stretching mode in substituted benzonitriles (148) shows that the frequency is independent of the nature of the solvent, but is dependent upon the electronegativity of the substituent. It was further shown that there was an approximately linear relationship between the log of the absolute intensity and the Hammett σ value of the substituent. Similar conclusions have been obtained from the band intensities of substituted anilines (149). On the other hand, in compounds of the type XC_6H_4COR the intensity of the CO group is very nearly independent of the nature of the substituent X although the CO frequency is displaced (150). Brown & Rogers (151) measured the integrated intensities of the OH group for a number of aliphatic alcohols and found it to depend upon the electron affinity of the alkyl substituent attached to the OH group, the intensity being greatest when the substituent is most electronegative. Stone & Thompson (152) have reported the band intensity and half-band width of the hydroxyl group in a number of phenols. Ferguson (153) has shown that the molar extinction coefficients at the band maxima of infrared "inactive" fundamentals of benzene in solution are markedly sensitive to the nature of the solvent. CS_2, bromobenzene, chlorobenzene, and pyridine enhance the inactive fundamentals, while CCl_4 and cyclohexane diminish the extinction coefficients below those observed in pure liquid benzene.

Hanson *et al.* (154) have calculated the intensities of rotation lines in absorption bands and Gallup (155) has considered the intensity distribution in the P and R branches of the fundamental bands of $C_{\infty v}$ molecules.

The induced infrared vibration-rotation bands of homonuclear diatomic molecules have been successfully interpreted as being due to the dipole moments induced by the intermolecular forces in a cluster of interacting molecules. The induced absorption is therefore markedly dependent on the separations between the interacting molecules. van Kranendonk (156) has calculated the intensity of these forbidden bands and its dependence on the density and temperature. The fundamental band of liquid and solid hydrogen has now been recorded with a grating spectrometer and new detail of structure obtained (157). The splitting of the Q branch increases with density of the perturbing gas and has been interpreted as being due to the participation in the absorption process of the relative kinetic energies of the collision partners (158). A study of the induced infrared absorption in gaseous acetylene under pressure has been reported by Minomura (159).

Solids and Large Molecules

The matrix isolation method holds immense promise for successful application to many problems associated with highly reactive molecular species. This method consists of dispersing the chemically reactive substance in a large excess of an inert material at a temperature sufficiently low to prevent migration and combination of the active species. Pimental and co-workers have used this technique to study the photolysis of HN_3 (160) and to investigate hydrogen bonding in water (161) and methyl alcohol (162). Fundamental vibrations were observed for monomeric, dimeric, and polymeric water molecules and it was concluded that the dimers were cyclic in structure. The OH stretching mode was used to identify monomer, dimer, trimer, tetramer, and high polymeric species in methanol. Here the dimer and trimer species appear to be cyclic while higher polymers have open chain structures.

Dows (163) obtained the spectrum of solid N_2O at $80°K$. As the N_2O crystal does not have a center of symmetry all frequencies are permitted in the Raman and infrared. However, in contrast to CO_2 (164) there is no evidence of splitting due to intermolecular coupling. The spectra of sublimed films of PH_4I and PD_4I at $-78°$ and $-190°$ show no evidence for phase transitions (165). Solid N_2O_4 was studied in polycrystalline films at $-180°$ (166) and the spectrum found to be consistent with the planar symmetric, V_h, structure reported from the x-ray investigation of the solid (167). From combination bands, it was deduced that at least two torsional lattice modes were in the range 18–30 cm.$^{-1}$ Snyder & Hisatsune (168) reported that the spectrum of N_2O_4 is not significantly changed either in the position of the bands or their intensity in passing from gas, to liquid, to solid. They agree with previous investigators that the molecule has the same structure in all phases. Jones has examined the vibrational spectra of several metal cyanide complexes in the solid state and concluded from force constant calculations that in $KAg(CN)_2$ (169), $KAu(CN)_2$ (170), and $Hg(CN)_2$ (171), the metal atom is bonded to the carbon atom rather than to the nitrogen atom. Polarized spectra of Rochelle salt were obtained with a prism-grating spectrometer by Baker & Webber (172). Analysis gave tentative locations for the hydrogen atoms.

Urea and thiourea have received attention from Stewart (173), Badger & Waldron (174) and Davies & Hopkins (175) while the spectra of urea and urea-d_4 have been reported by Mizushima and co-workers (176). The guanidinium ion has been reported by Angell *et al.* (177). Hornig and co-workers have enlarged their work on the spectra of crystals to publish on boric acid (178) and HX-DX mixed crystals (179). No evidence for proton disorder was found in boric acid which leaves the shape of the heat capacity curve for this substance still unexplained. The mixed halide crystals were demonstrated to exist in linear zig-zag chains. Other crystals investigated include $NaNO_2$, KNO_2, and $AgNO_2$ (180), sulfamic acid and sodium and potassium sulfamate (181).

Ferguson (182), using deuterobenezene, has confirmed a previous conclusion (183) that the symmetry of the benzene-iodine charge transfer complex is C_{6v}. Earlier work of Collin & D'Or (184) in which certain broad intense bands in solutions of bromine or chlorine in benzene were attributed to halogen-halogen vibrations in a charge-transfer complex have been confirmed by Person *et al.* (185). Kross & Fassel (186) have reported on some regularities in the spectra of picric acid molecular complexes. It was found that the asymmetric stretching mode of the nitro group and the out-of-plane bending vibration of the picric acid component are sensitive to complex formation. These sensitivities correlate with the type of charge transfer complex formed. The spectra of the metal chelate compounds of *o*-hydroxyazobenzene lose the OH band at 3300 cm.$^{-1}$ and show a bathochromic shift of the carbonyl band at 1600 cm.$^{-1}$ (187). The order of the shift being $Cu > Ni > Co$. Other metal chelates reported include those of 1,3-diketones (188). Phillippe & Hobbs studied the association of phenol with several ketones (189). Quagliano and co-workers have continued their study of inorganic coordination complexes (190, 191, 192, 193). Other studies on complexes which might be mentioned include a comparison of the spectra of unidentate and bidentate metallic complexes (194), nitrato complexes (195), thiourea-alkali halide complexes (196), addition compounds of aluminum chloride with acetyl and mesityl chlorides (197), and the addition compound of BF_3 with acetyl fluoride (198).

Hexter & Goldfarb (199) have carried out an interesting study of *o*-quinol clathrate compounds.

Infrared spectroscopy has been used so widely and successfully in studying molecular structure in different environments that it might almost be regarded as the tool *par excellence* for such studies. It is not surprising, therefore, that increasing attention should be devoted to studies of the infrared spectroscopy of the adsorbed state. Such studies are complicated by several difficulties such as pronounced scattering of radiation by the adsorbent and unambiguous interpretation of the results. Where such difficulties can be eliminated or largely overcome, it can confidently be expected that study of the infrared spectra of the adsorbed phase will throw new light and give deeper insight into the nature of the perturbations of the adsorbate by the surface of the adsorbent. What can be accomplished in this direction is indicated by work done during the year under review.

Sheppard & Yates (200) studied the infrared spectra of CH_4, C_2H_2, C_2H_4, and H_2 physically adsorbed on porous silica glass and noticed that bands found in the gas phase were shifted in the adsorbed state. In addition, the perturbing effect of the adsorbed surface was dramatically demonstrated by the presence of new bands which for reasons of symmetry are forbidden in the unperturbed molecules in the gaseous state. In the case of methane, although a grating instrument was used, rotational fine structure could not be resolved. However, the shape of the antisymmetric ν_3 band is inconsistent with a three dimensional free rotation, but is explainable on the assumption

of free rotation of the molecule about an axis perpendicular to the surface.

Outgassed Aerosil shows a sharp band at 3749 cm.$^{-1}$ which is attributed to the 0–1 transition of the stretching frequency of surface hydroxyl groups (201). When molecules are adsorbed adjacent to these, the 3749 cm.$^{-1}$ band diminishes and a new one appears at a lower frequency. The magnitude of the shift is a measure of the interaction between surface OH groups and the adsorbate while the residual intensity of 3749 cm.$^{-1}$ band is a measure of the free surface groups remaining.

Infrared studies can also provide information on new species formed during chemisorption. Thus Young & Garland (202) have carried out extensive studies on carbon monoxide chemisorbed on rhodium and concluded that three types of surface species are formed. The reaction of chemisorbed CO with O_2, H_2 and H_2O was investigated spectroscopically and the results interpreted in terms of these CO surface species.

Bent & Crawford (203) have demonstrated that dispersion in potassium halide pellets appears to be a safe and convenient way to study spectroscopically the decomposition of unstable substances. They used this method to follow the decomposition of di-t-butyl peroxide and determine the rate of scission of the O—O bond. Greenler (204) has described an interferometric infrared spectrometer. Duval (205) has studied amino acids in one drop of aqueous solution, and Schrader *et al.* (206) are able to obtain the Raman spectrum of a compressed solid with one-third of a cubic centimeter of material. Pemsler (207) emphasizes the advantages of obtaining derivative spectra directly in analyzing overlapping bands.

That only about half of the 450 papers read by the reviewers appear in the bibliography is due not only to limitations of space but also to personal interest. It is quite likely that a list of omissions would include some important papers and to the authors of these the reviewers offer an apology.

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EXPERIMENTAL MOLECULAR STRUCTURE[1]

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Introduction

In writing a review chapter of about ten thousand words on a subject with such an all-embracing title as that of the present one the authors have two choices: These are to list titles of papers bearing on the subject which have appeared since the last such review was written, or to select from the broad field several regions that are of particular interest to them and attempt to write more definitive reviews of the status of the special subjects. We have chosen the second course.

A number of years has elapsed since a general review of the status of the electron diffraction method for determining the structures of gaseous molecules has appeared in these volumes, and no review of the subject of electron diffraction by solids has hitherto been presented.

One of the well defined trends in structure determinations in recent years is the increased confidence of the experimenter in the accuracy of his structure determination. Interatomic distances are very frequently reported with four significant figures. This kind of accuracy requires that care be taken to indicate the nature of the distance reported, since in general each experimental method leads to its own characteristic average of the distance over the omnipresent motions of the nuclei. The short sections on structure determinations by the nuclear magnetic resonance technique and on the current status of our knowledge of carbon-hydrogen distances were written with the object of illustrating the care that must be exerted by the casual reader in interpreting reported structures and in comparing the results obtained by different methods. We would like these sections to serve as reminders to authors that great care should be taken to indicate the nature of the distance they report and that the accuracy of the distance, not its precision, is of interest to the general reader.

It has been generally announced (1) that Sutton and co-workers are engaged in a considerable revision and expansion of the tabulation of interatomic distances [Allen & Sutton (2)] as obtained by all physical methods. Thus we have felt no need to attempt any general compilation of recent structural information. However, in surveying the literature of the past two years, the results of certain works attracted our attention, usually because the results did not agree with our preconceived ideas. These we logically (!) designate "unusual structures" and comment on briefly in the final section of this chapter.

Electron Diffraction

In this section recent progress in electron diffraction techniques for investigations of the structures of gases and solids will be reviewed. This seems

[1] The survey of literature pertaining to this review was concluded November, 1957.

appropriate for the reasons given in the introduction and also because a highly informative and interesting symposium on Electron Diffraction Studies of Solids and Gases was held at Montreal in July, 1957 (3).

Electron diffraction by gases.—Because of the many reviews (4, 5) on the subject, it seems unnecessary to discuss in much detail the fundamentals of diffraction of electrons by gases. However, for purposes of orientation and of later discussion we offer a very concise and somewhat oversimplified intro- duction. The electron diffraction method is one in which a highly collimated, mono-energetic beam of electrons of wavelength approximately 0.05 A is diffracted by a fine jet of gas molecules, and the resultant diffraction pattern is recorded on a photographic plate. Such a diffraction pattern has the molecular scattering of interest superimposed on a rapidly decreasing back- ground of atomic and incoherent scattering; this background decreases so rapidly as to preclude the profitable use of a microphotometer for the measurement of the intensity of the molecular scattering function. Under these conditions the molecular scattering function must be perceived visually, the eye being able to discern changes in intensity even on a rapidly decreasing background. In this way qualitative information on the relative intensities and the shapes of the various features of the molecular scattering function is obtained. However, the visual method requires both skill and practice; some investigators have been far more successful with it than have others. An important advance in the measurement of the intensity of the molecular scattering function has been the development of the sector method by the Norwegian school (6, 7, 8). In this method a rotating sector is interposed between the point of diffraction and the plate. It is shaped in such a way as to compensate approximately for the rapid decrease in intensity with in- creasing angles of scattering (distances out from the center of the photo- graphic plate). The compensated diffraction pattern, which now contains the molecular scattering function superimposed on a relatively flat back- ground, can be interpreted with the aid of a microphotometer.

The procedures for the determination of the details of the molecular structure from the molecular scattering function may vary with the complex- ity of the molecule and with the investigator. Generally, a radial distribution function (9) is computed from the scattering function. This distribution function, if properly interpreted, yields in effect the probability distribu- tion of interatomic distances in the molecule. In the case of simple structures such a distribution function is usually sufficient to lead to a determination of the structure; in cases where peaks overlap on the distribution function it may be necessary to accept or reject a model of the structure on the basis of agreement between observed and calculated intensities of scattering.

In the past several years remarkable advances have been made in the electron diffraction method. The major theoretical advance has been the rejection of the first Born approximation as a universally applicable approxi- mation for the calculation of the intensity function. In this approximation it is assumed that the incoming electron wave is not much diffracted by the scattering center, and this assumption leads to only real values of the atomic

scattering amplitudes. Schomaker & Glauber (10) pointed out that if one rejects this approximation and assumes the atomic scattering amplitudes to be complex, then the anomalies found by electron diffraction in the structures of certain heavy atom-light atom compounds, e.g, UF_6 (11), can be explained. Previous explanations involved the postulate of asymmetric structures for such molecules, despite ample evidence from other physical methods that such structures were indeed symmetric. Glauber & Schomaker (12) derived approximate complex atomic scattering factors from the screened coulomb field and a second Born approximation method. These scattering factors later proved to be inadequate to explain the variation with wavelength of electron diffraction patterns of UF_6. A satisfactory explanation of the wavelength variation was achieved with complex atomic scattering factors computed by Hoerni & Ibers (13) from the partial waves scattering theory using the Thomas-Fermi field for the uranium atom and the Hartree field for the fluorine atom. Using the Thomas-Fermi field, these calculations were later extended to other atoms (14). Schomaker (15) has indicated that these complex scattering factors appear to be satisfactory for the physically reasonable interpretation of the diffraction patterns from a number of other heavy atom-light atom compounds. There can be no doubt at this time that failure of the first Born approximation is the explanation of the apparent asymmetries found formerly by electron diffraction for many heavy atom-light atom compounds. It is to be emphasized, however, that the present visual data on these compounds provide a sensitive test of theoretical scattering factors only at those scattering angles where the difference in phase of the atomic scattering functions of the heavy and light atoms is approximately 90°. More sensitive tests must await the collection of sector data. The complex atomic scattering factors of Hoerni & Ibers are based on the rather drastic approximation of the Thomas-Fermi field. Undoubtedly the calculations could be made more reliable with the use of the Thomas-Fermi-Dirac (16) field, but what are really needed are self-consistent fields for the individual atoms. Although self-consistent fields are, as yet, unavailable for most atoms, there is reason to believe that the ready availability of high-speed computers will lead to increased interest in such calculations (17).

The major experimental advance of the past few years has, of course, been the development at Oslo of the rotating sector method. The original suggestion for a sector was made by Trendelenburg (18) in 1933, but it was not until shortly before World War II that the technique was perfected at Oslo. After the war the Oslo group under Finbak and Hassel began actively to utilize sector data in the determination of molecular structures. The quality and reproducibility of these data have been so high as to provide a real impetus for other diffraction centers to build sector cameras. The use of the sector camera has also provided impetus for experimental improvements which have been useful as well in nonsector work. Thus, advances have been made in the control of the high voltage, the vacuum, and the nozzle systems of electron diffraction cameras, with the result that the scattering angle over which both sector and nonsector data can be recorded has, in favorable

cases, been doubled. The experimental and procedural methods used in connection with sector cameras have been discussed in detail by Hassel & Viervoll (7), Bastiansen (8), Karle & Karle (19, 20, 21), Bauer and his co-workers (22, 23), and by Brockway and his co-workers (24, 25). These papers present wide differences of opinion, and so some discussion of the sector method would seem warranted.

Sector data are to be preferred to visual data because they provide much more than a qualitative comparison of adjacent features of the intensity function. However, there is still much justification for the use of both visual and sector data (22, 23), for the eye is able to detect with greater sensitivity some portions of the diffraction record; and, moreover, visual data provide a check on the broader features of the sector data. Unfortunately, most laboratories use sector data exclusively.

It is to be emphasized that the background problem is not eliminated with the use of the sector. Karle & Karle (20) have proposed a method, essentially one of successive approximations, based upon the criterion of non-negativeness of the radial distribution function, for the location of the proper background curve. Their method will only work, however, if the proper theoretical expressions for the scattering are employed and if an approximately correct structure has been found. For example, the background will be a function of the scattering factors used (23) and of the correctness of the structure. Moreover, Waser & Schomaker (26) have pointed out that perhaps other criteria, in addition to non-negativeness, are required. The most straightforward method for the location of the background curve is perhaps the simple appeal to intuition as employed by Bastiansen [Almenningen & Bastiansen (27)]. The important fact about the background is that it need not be strictly correct as long as it is not in error in an unsmooth way. The effects on the radial distribution function of errors in the background, as well as other factors such as the limitation of data, can be predicted with the aid of the folding theorem of Fourier analysis. Waser & Schomaker (26) have given a lucid and highly informative discussion of this theorem and its application to the Fourier inversion of diffraction data. It is to be regretted that this exceedingly important paper seems to have been overlooked by both electron and x-ray diffractionists.

The utilization of sector data varies from laboratory to laboratory. Bastiansen, for example, determines his structures strictly from the radial distribution function with no appeal to intensity functions. On the other hand, he, unlike other workers, does not attempt in general to determine the mean-square amplitudes of vibration from his radial distribution functions (see below). Other workers to a varying degree ultimately reject or accept their structural models on the basis of the agreement between observed and calculated intensity data. There is much to recommend this procedure in the case of complex molecules, for not only may some intensity features be quite sensitive to small variations in molecular parameters, but also the use of intensity functions allows the utilization of a least-squares procedure, such as that described by Hamilton & Schomaker (28), for the

refinement of the structure and for the establishment of meaningful limits of error.

The Karles were the first to attempt to obtain from sector data mean-square amplitudes of vibration [more properly, the average of the square of the amplitudes projected on the line joining the pair of atoms in their equilibrium position (20)]. These attempts have not been overly successful; thus, there are significant differences between the Karles' amplitudes for CCl_4 (19) and those of Bartell, Brockway & Schwendeman (25). Moreover, the agreement with theoretical values derived from normal coordinate treatments has not been too good in general [compare observed results (21) for CH_2CF_2 and CF_2CF_2 with theory (29)]. There are, of course, reasons for this poor agreement. The mean-square amplitudes are derived from the shapes of the peaks on the radial distribution function. Many of the factors, the complex nature of the scattering amplitudes (30), difficulties in background determination, etc., which are tacitly assumed not to affect significantly the positions of the peaks on the distribution function, will affect the shapes of the peaks. It seems to us that to attempt to derive mean-square amplitudes of vibration from electron diffraction data is perhaps a mistake, for more accurate amplitudes can be computed from spectroscopic data for simple substances [Morino, Kuchitsu & Shimanouchi (29)], and from various approximations [Morino *et al.* (31)] for complex substances, and these could be employed as input data in electron diffraction studies. Moreover, in deriving mean-square amplitudes from electron diffraction data the assumption is made that the vibrations are harmonic; this assumption is a questionable one. For example, Bartell, Brockway, & Schwendeman (25) have shown that the effects of anharmonicity on the thermal vibrations are sufficiently large in CCl_4 to cause detectable frequency modulation of the observed intensity function.[2]

The various assumptions about the effects of motion probably lead to derived distances reliable within the stated limits of error, but surely not to amplitudes of vibration reliable within the limits of error which have been given. However, it seems to these reviewers that much of a theoretical and practical nature still remains to be done in electron diffraction studies of simple molecules before the limits of error stated by some workers for their electron diffraction determinations can be accepted without reservation. It would be highly desirable to compute the intensity and radial distribution functions for a simple substance, say methane, taking into account not only the internal motions (with due consideration to anharmonicity) of the molecule, but also reliable values of the complex atomic scattering factors as computed from exact (hydrogen) or Hartree Fock (carbon) fields. Moreover, it would be desirable to compare the derived background with that computed from reliable incoherent scattering functions, such as that for carbon

[2] We have just seen the preliminary account of the study of the vibrations in benzene by Bastiansen & Cyvin (115). The usual assumption is made that the vibrations are harmonic, and only the mean-square amplitudes are obtained from the electron diffraction data and compared with values derived from spectroscopic data. The agreement is very good.

given by Keating & Vineyard (32). These comparisons would surely lead to a better understanding of the nature of the many approximations, both theoretical and experimental, which at present are assumed valid in electron diffraction.

If it should be true that distances are being determined within the limits of error stated [e.g., ± 0.004 A in CCl_4 (25)], then it becomes important to state explicitly what motion-averages of these distances are being determined. Bartell (33) has considered this problem to some extent, but in detail only for diatomic molecules. Some consideration of the problem as it applies to CCl_4 has also been given (25). However, such problems are probably best treated from the point of view of a normal coordinate analysis.

Finally, the reviewers want to emphasize that despite what they consider to be incomplete, and in some cases improper, utilization of the data available, the electron diffraction method is still the most generally applicable one for the determination of the structures of gaseous molecules.

Determination of crystal structures by electron diffraction.—In the last few years rapid progress has been made in the application of electron diffraction to the determination of crystal structures. Our purpose here is to discuss briefly the techniques employed, the results obtained, and the theoretical and experimental problems which remain unsolved or unresolved in this new field. We shall discuss neither the study of amorphous solids by electron diffraction, such studies being akin to the gas diffraction work; nor the diffraction of slow electrons as pursued by Farnsworth and co-workers (e.g., 34), and by others; nor what might be called the classical electron diffraction studies of solids as described by Thomsen & Cochrane (35).

There are some quite important reasons for applying electron diffraction to the study of crystal structures, reasons which often make the technique complementary to x-ray diffraction techniques [Rees (36)]. The most important reason is that electron diffraction is an effective technique for the study of minute single crystals, crystals so small as to appear essentially amorphous to x-rays. Crystals need only be of a thickness parallel to the electron beam of some tens of Angstroms in order to give useful diffraction patterns. Electron diffraction is thus a valuable tool for the study of materials, which either by their location (e.g., on surfaces) or by their limited quantity, are unavailable for x-ray study. Moreover, the study of minute single crystals is of great interest for such crystals generally owe their small size to the occurrence of stacking faults, dislocations, etc. Another important application of electron diffraction is in the location of light atoms since the lighter atoms in relation to the heavier ones scatter electrons relatively more effectively than they do x-rays.

The developments which have made possible the general study of structures of crystalline solids by electron diffraction are primarily electron-optical in nature, and have come about largely from experience gained in the development of commercial electron microscopes. The modern electron diffraction instrument is often as complicated as the more complex electron microscopes, demanding the same degree of electronic stability and the same

precision of machining. A typical instrument designed for crystal-structure work incorporates a high intensity electron gun (voltage range perhaps 30 to 100 kev); a double condenser system to provide minimum effective source size and hence maximum resolution; a specimen holder designed to allow convenient and controlled manipulation of the specimen; an objective lens, often of the asymmetric design to allow room for manipulation of the specimen as well as a short specimen to objective lens distance; a double projector system to allow for microscopy in addition to diffraction; and a recording system. Microscopy facilities are included to make it easier to locate suitable crystals; high resolution microscopy is not required. The commercial electron microscope is designed for maximum resolution, and in such an instrument in order that spherical aberration be minimized the distance from specimen to objective lens is minimized, the specimen in most designs being inserted into the objective lens. Such a design feature offers little hope for specimen manipulation and so is a great inconvenience if one wishes to do diffraction. Since commercial electron microscopes are usually difficult to redesign, they are not convenient for use in electron diffraction. Unfortunately, no commercially available electron diffraction instrument is designed for crystal-structure analysis. For this reason most electron diffraction instruments for use in this field are made in the laboratory, the instrument of Tanaka & Hashimoto (37) being typical of the more advanced design described above. It is to be emphasized, however, that if one maintains the same electron-optical stability, much simpler systems can be employed to carry out studies of crystal structures, at the sacrifice of microscopy and of general versatility. A simpler instrument has been described by Cowley & Rees (38), although this instrument has been superseded by a more complex and versatile one.

The use of electron diffraction for crystal-structure analyses has been pioneered by two major groups: Cowley and Rees, in Melbourne, who have concentrated on single-crystal techniques, and Pinkser and his co-workers, particularly Vainstein, in Moscow, who have concentrated on polycrystallite techniques. The earlier Russian work is well summarized in Pinsker's (39) book, and the recent work is summarized in the, as yet untranslated, book of Vainstein (40). It should be noted that with the proposed translation into English of the Russian crystallographic journal, *Kristallographiya*, Russian developments in electron diffraction should be much easier to follow.

The determination of crystal structures by electron diffraction has usually depended upon the assumption that the intensities obtained are proportional to the square of the structure amplitudes (the kinematic approximation, which we discuss below) and upon this assumption the usual methods of x-ray structure analysis, including Patterson and Fourier syntheses, have been employed [Cowley (41)]. In this way many interesting structure analyses have been carried out in the last few years, and we offer a summary of a few of these in order to illustrate the versatility and applicability of the method. The hydrogen positions and the stacking order in boric acid have been determined by Cowley (42). In contrast to the electron diffraction results, the x-ray results of Zachariasen (43), and indeed the spectroscopic evidence

of Hornig & Plumb (44), support an ordered structure for boric acid. It is possible, however, that both structures are correct, the size and history of the boric acid crystals being so different; the matter clearly needs further study. Cowley (45) has studied the structure of basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, and has found the light atoms (carbon and oxygen) to be clearly resolved in the presence of the lead atoms, and on this basis has proposed a probable structure. The unit cell found by Cowley has recently been confirmed by Katz & Reed (46) in an x-ray study. An illustration of the complementary use of x-ray and electron diffraction is afforded by the study of the structures of graphite-ferric chloride compounds by Cowley & Ibers (47), in which electron diffraction data provided information on the structures of the layers, and x-ray data provided information on how such layers were stacked. The work of Moodie (48, 49) on the effects of heating gold in air is a good illustration of the study of the structures of single crystals projecting from surfaces. Moodie finds that if the gold contains traces of copper, then spines of CuO form normal to the gold surface when the gold is heated in air. The work of Vainstein (50) on diketopiperazine, in which he confirms the essentials of the structure found earlier by Corey (51) from x-ray work, and in addition locates the hydrogens, is a good illustration of the use of electron diffraction in the study of crystal structures of organic substances. Electron diffraction has also proved quite useful in the characterization of the structures and transformations of alloys. For example, Takahashi & Mihama (52) prepared samples of Al-Cu by vacuum evaporation of the elements on a cleaved face of NaCl. They then studied by microscopy and diffraction the transformations which occur when such samples are heated. The transformations $Al_2Cu \rightarrow AlCu \rightarrow Al_4Cu_9 \rightarrow AlCu_3$ were found, and the relative crystallographic orientations between each phase permitted a mechanism for the transformations to be proposed. Ogawa & Watanabe (53) have studied several ordered alloys, including Au_3Mn for which they have found a remarkable antiphase domain structure. Work such as this is exceedingly important for our understanding of the metallic state.

The major experimental problems associated with studies such as these can be summarized very briefly as involving the preparation and manipulation of the specimen, and the observation and recording of the diffraction pattern. These problems are not particularly pressing at this time. There are many interesting studies still to be carried out on crystals of convenient habit. Various methods for habit modification, for example, epitaxy (54) and preferential adsorption (55), might be of great help in the future. The selection of the diffraction pattern by observation on a fluorescent screen leaves much to be desired in terms of detail, but the rapid development of image intensifiers (56) offers much hope in this regard. The photographic method for the recording of diffraction patterns, though generally satisfactory, might well be replaced eventually by xerographic methods (57), or perhaps by perfected crystal methods based on the work of Takagi & Suzuki (58).

We must emphasize, however, that the major problems associated with the study of crystal structures by electron diffraction are theoretical rather

than practical. The wide range of applicability of the kinematic theory as found by Yamzin & Pinsker (59) has now been challenged by Lennander (60) and by Kuwabara (61). The past success of electron diffraction in structure determinations is probably due in large measure to the fact that real crystals are usually imperfect, and that such imperfection extends the range of applicability of the kinematic theory. On the other hand, it is possible that many of the effects attributed to crystal imperfections in previous studies actually result from the failure of the kinematic approximation. A number of factors which affect the interpretation of electron diffraction intensities and which have often been neglected in the past were discussed at the Montreal symposium (3). It became clear that further theoretical work on interaction of electrons with imperfect as well as perfect crystals is needed. [See Cowley & Moodie (62) for a new theoretical approach to the scattering of electrons.] Two quite promising methods for deriving kinematic intensities from the observed intensities were presented at Montreal. One by Honjo & Kitamura (63) involves the extrapolation of observed intensities to zero wavelength, and this method is apt to spur further development of high voltage electron diffraction instruments. Another method by Nagakura (64) involves the use of intensity statistics. These methods coupled with our increased knowledge of the effects of failures of the various approximations made in the past assure the continued successful application of electron diffraction techniques to structure problems. It is probably true, however, that one important application of electron diffraction, namely, to the study of crystal imperfections, must await further theoretical developments.[3]

LIMITATIONS OF THE SECOND-MOMENT METHOD

The second moments of nuclear magnetic resonance (nmr) spectral lines from crystals when combined with the necessary crystallographic data provide an attractive method for the location of certain nuclei, particularly protons [Andrew (65)]. Since the limitations on the accuracy of this method have not been considered in previous reviews, we do this here. The experimental difficulties of the method have been outlined by Wertz (66) and will not be considered further. Rather we wish to consider the limitations imposed on the method by inadequate crystallographic data and by inadequate knowledge of the effects of motion on the second moments.

It is important, first of all, to distinguish three classes of substances. In the first class are those substances whose second moments result almost entirely from intramolecular contributions. In the second class are those substances for which the contributions of the intermolecular terms to the second moments are important. In the third class are those substances for which essentially no crystallographic data are available. It is often possible to include some type of motion correction in studies of a substance belonging

[3] This manuscript was completed before we saw a discussion in terms of the dynamic theory (but, unfortunately, with the neglect of absorption) by Whelan & Hirsch (116) of the diffraction of electrons from crystals containing stacking faults. A partial test of the theory is described in a second paper (117).

to the first class; moreover, a precise knowledge of the crystal structure is not essential. For these reasons internuclear distances can be determined with the greatest accuracy here, and most of our discussion will be concerned with such determinations. Unavailability of precise crystallographic data and especially the inability to correct for motion the significant inter-molecular contributions to the second moments preclude, generally, the determination of accurate internuclear distances in a substance belonging to the second class. Even the ingenious, isotopic-substitution method which Andrew & Eades (67) applied to crystalline benzene in order to separate inter- from intramolecular contributions is strictly valid only for a rigid lattice. A rigid lattice is an idealization which is unobtainable in practice; the effects of zero-point energy vibrations on the second moments can be quite important. It is often impossible to determine even broad features of a molecular arrangement, for example, to distinguish *trans* from *gauche* configurations, in a substance belonging to the third class. For such substances the second-moment method is apt to yield no useful answers to molecular structure problems; see, for example, the recent work of Gutowsky & Takeda (68) on the symmetry of substituted fluoroethanes.

It is to be emphasized that many, in fact most, second-moment studies have included no corrections to the derived distances for the effects of zero-point energy vibrations. For this reason it is important to interpret the limits of error on bond distances derived in such studies as measures of precision rather than as measures of accuracy. The neglect of the effects of motion is one reason why, in those still rather rare cases where the results of second-moment studies can be compared with the results of other physical methods, agreement is often poor. Of course, because of motion perfect agreement is not expected; the second-moment method yields a different motion-average of the internuclear distance from those of other physical methods. This fact further supports our contention that it is important to state what type of average distance is being obtained in a given structure determination. The NH bond length in urea provides an example of poor agreement. Worsham, Levy & Peterson (69) recently studied single crystals of urea by neutron diffraction and derived an NH distance of 0.99 ± 0.02 A. Andrew & Hyndman (70) from nuclear magnetic resonance studies of single crystals obtained the distance 1.046 ± 0.01 A. Another nuclear magnetic resonance determination of this distance has been made by Krombout & Moulton (71) from a study of a powder specimen. They apparently obtain the result that the NH distance is 1.010 ± 0.007 A on the assumption [which is correct (69)] that the HNH angle is close to 120°. The difference between the two studies could possibly be systematic, for large single crystals and powders can differ significantly with regard to ordering, impurities, and other factors. However, it is not clear if this particular difference is significant for Krombout & Moulton "revise" their NH distance determination to 1.036 ± 0.009 A in a note added in proof. Discounting their results, one still must attempt to explain the apparently significant differences between a neutron diffraction result of 0.99 ± 0.02 A and the nuclear magnetic resonance result of 1.046

±0.01 A for the NH distance in urea. We have indicated above that part of this difference could result from the neglect in the nmr study of the effects of motion. Moreover, the nuclear magnetic resonance spectra were obtained at room temperature, and it is possible that additional motional narrowing of the second moment has occurred; such narrowing will result in too large a distance being derived. On the other hand Worsham, Levy & Peterson (69) point out that the correction of their derived distance for motion is exceedingly difficult and that the distance given must be considered a lower limit to the true distance. Thus both results must be interpreted with some caution, and it is not clear whether a real discrepancy does exist. Unfortunately, the NH distance in urea remains in doubt.

Although it is true that some attempts have been made to correct the second moments for the effects of motion, it is also true that there has been a remarkable lack of agreement in the manner in which such corrections have been made. As a result the intercomparisons of reported distances as determined by the nuclear magnetic resonance method are rendered quite difficult. By way of illustration we may consider the results of determinations of the NH distances in powder specimens of ammonium chloride, ammonium fluoride, and hydrazinium fluoride (Table I). In the original study of ammonium chloride (72) no account was taken of motion and an NH distance of 1.025 ± 0.01 A was derived. In a later study Gutowsky, Pake & Bersohn (73) took account of the librational motion of the ammonium ion about its

TABLE I

ORIGINAL AND REVISED NH DISTANCES

Substance	Original Distance (A)	Revised Distance (A)	Temperature °C.	Ref.
NH_4Cl	1.038 ± 0.004	1.032 ± 0.004	-195	(73)
NH_4F	1.042 ± 0.01	1.041 ± 0.017	-75	(74)
$N_2H_6F_2$	1.075 ± 0.02	1.050 ± 0.028	-180	(75)

lattice site but neglected the effects of internal stretching and bending of the ion. Drain (74) made a similar approximate treatment of the ammonium fluoride data. Deeley & Richards (75) on the other hand ignored the effects of librational motions of the hydrazinium ion and considered only the effects of the stretching and bending motions of the ion. The present authors (76) have made a detailed study of the effects of the various motions on the second moments of the proton magnetic resonance lines in these three compounds. From preliminary calculations on methane, for which sufficient detailed spectroscopic data are available, it was concluded that the valence bond approximation to the general five-constant potential function is sufficiently accurate for the treatment of the internal motions of the ammonium ion. Because of the symmetric nature of the potential restricting bending it is appropriate to neglect the anharmonicity of this motion. However, anhar-

monicity of the pure stretching motion cannot be neglected, for the unsymmetrical nature of the stretching potential function results in the first moment of the amplitude being comparable in magnitude to the root-mean-square amplitude of the variation of the internuclear distance. This type of normal coordinate treatment could not be applied to the motions of the hydrazinium ion because of the general complexity of the molecules and because of the paucity of infrared and Raman data. Nevertheless, an approximate treatment, shown to be sound by prior application to the ammonium ion, was applied. In Table I are shown the original and revised values of the NH distances. In the cases of ammonium chloride and hydrazinium fluoride the changes are greater than the errors estimated in the previous determinations. We might add that the changes seem quite reasonable in view of the relatively large difference in the NH-stretching frequencies in NH_4Cl and NH_4F and in view of the similarity in bonding (N—H—F) in NH_4F and $N_2H_6F_2$. The increases in the estimated errors have come about not only by consideration of the uncertainties of the applied motional corrections, but also by a more careful consideration of the crystallographic uncertainties.

In conclusion we recognize that the applications of nuclear magnetic resonance to problems of molecular structure and motion have been extensive and in many cases unique, and no attempt has been made here to discount the importance of the technique in the study of the solid state. Yet as a means of determining accurate internuclear distances in solids the second-moment method is more limited than might be supposed from a casual reading of the literature.

CARBON-HYDROGEN DISTANCES

Inherently, the most precise data on the conformation of gaseous molecules are those derived from the spacing of rotational energy levels. The information that is obtained, be it from the interpretation of vibration-rotation bands of infrared spectra, pure rotation Raman spectra, or pure rotation microwave spectra, is the average of reciprocal moments of inertia for particular states of vibration of the molecule, usually the ground state. These moments of the reciprocal moments of inertia are exceedingly complex functions of the various moments of the internuclear distances in the molecule. It has been the long standing custom of spectroscopists to calculate from the moments of inertia of the oscillating molecule the apparent internuclear distances and bond angles of the corresponding rigid rotator. Although it has been recognized that this approximation introduces characteristic uncertainties in the molecular structures that are so obtained, these uncertainties are rarely reflected in the reported limits of error. The magnitude of these uncertainties increases with lightness of the atoms involved, and in the cases of distances involving hydrogen (or deuterium) atoms the error resulting from this approximation becomes very large compared to the accuracy with which the rotational constants are measured. In view of the large number of papers in which have been reported structures of molecules containing

hydrogen atoms, a number that has increased greatly during the past two years, it appears that now is an appropriate time to examine the present status of our knowledge of distances involving hydrogen atoms.

For many years structure chemists were content in the belief that the length of the saturated carbon-hydrogen bond could be taken equal to the equivalent rigid-rotator distance,[4] $r_o(CH) = 1.093$ A, found by Ginsburg & Barker (77) in their study of CH_3D. This value of $r_o(CH)$ was confirmed by Childs' (78) analysis of Cooley's (79) data on CH_4. Electron diffraction patterns of hydrocarbons and their derivatives were interpreted with the assumption that the CH distance always has the value 1.09 A. Perhaps the best example of the faith in this assumption is to be found in Herzberg's (80) discussion of the significance of the values of the rotation constants A_o found from the infrared spectra of the compounds CH_3F, CH_3Cl, CH_3Br, CH_3I, and CH_3CH_3. The moment of inertia $I_A{}^{\circ}$ of the methyl group in these compounds is 3 per cent greater than I° of CH_4. Herzberg (80) attributed the entire increase of $I_A{}^{\circ}$ in these compounds to an increase of the angle HCH from its tetrahedral value 109.5 to ca. $112.0 \pm 0.2°$.

In recent years doubt has arisen concerning the validity of this assumption of invariance of the saturated carbon-hydrogen bond distance. The rotational constants B_o from the microwave spectra of the methyl and trideuteromethyl halides have been combined with the values of A_o obtained for these compounds from their infrared vibration-rotation spectra to give values of $r_o(CH)$ decreasing from 1.109 A (CH_3F) to 1.100 A (CH_3I) and values of $\angle$ HCH increasing from 110.0° (CH_3F) to 111.0° (CH_3I) (81). Because of these results many authors are now inclined to the use of $r(CH) = 1.10$ to 1.11 as an assumed distance if the excess of parameters over data requires that certain distances be assumed in order for a structure analysis to be completed. Yet, there is no unanimity with regard to this assumption among the various structure laboratories [cf. 1.110 A (82) and 1.093 A (83)]. Furthermore, all methyl compounds do not show such "large" $r_o(CH)$ as the methyl halides. The rotational constants of many methyl derivatives have been interpreted to indicate $r_o(CH)$ in the range 1.086 to 1.097 A (see Table II).

The measures of internuclear distances that are of theoretical interest are, of course, r_e, the equilibrium distances corresponding to the minima on the potential energy hypersurface of the molecule. These equilibrium internuclear distances are related by the usual expressions to the moments of inertia of the rigid rotator with rotational constants A_e, B_e, and C_e which are in turn related to the observed ground state rotational constants by expressions of the form (84)

$$A_o = A_e + \frac{1}{2} \sum_{i=1}^{3N-6} \alpha_i,$$

where the α_i are constants characteristic of the various normal modes of vibration (i). These constants can be evaluated empirically (in principle)

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[4] We use the notation of Herzberg (80).

TABLE II[*]

CH STRETCHING FREQUENCIES AND r_o(CH) IN METHYL DERIVATIVES

Molecule	ν,cm.$^{-1}$			r_o, A
	$\parallel$	$\perp$	Avg.	
Methane	2914	3020	2994	1.093
Methyl fluoride	2964	2982	2977	1.109
Methyl chloride	2966	3042	3023	1.103
Methyl bromide	2972	3056	3035	1.101
Methyl iodide	2970	3060	3038	1.100
Methyl acetylene	2941	2994	2977	1.097
Methyl isocyanide	2951	3002	2985	1.094
Methyl cyanide	2942	2999	2985	1.092
Acetaldehyde	2710	$\begin{cases} 2915 \\ 2964 \end{cases}$	2863	1.086

* The data for all substances other than acetaldehyde (91, 92) are taken from Herzberg (80) and Gordy *et al.* (81).

from the analysis of the rotational structure of the vibration-rotation bands in the infrared or of the pure rotation spectra of vibrationally excited molecules. The only polyatomic molecules for which all α_i and thus r_e's have been evaluated are acetylene, hydrogen cyanide, carbon dioxide, and water (80), and hydrogen sulfide (85).

Alternatively it is possible, in principle, to express the α_i as functions of the moments of the normal coordinates, and thus to calculate these quantities from knowledge of the fundamental frequencies and their anharmonicities (84). There are indications that Lawrance & Strandberg (86) carried out some such calculation in their interpretation of the microwave spectra of various isotopic species of formaldehyde. However, this is the only molecule for which we can find evidence that such calculations have been made.[5]

The results of these two evaluations of r_e(CH) do not provide a clear guide to what may be expected in general. Thus for acetylene Herzberg (80) reports r_e(CH) $= r_o$(CH) $= 1.059_7$ A, while Lawrance & Strandberg (86) report for formaldehyde a CH distance (presumably r_e) of 1.12 ± 0.01 A, 0.03 A greater than the r_o(CH) $= 1.09$ A (87, 88) found for this substance.

The present authors have employed an adaptation of Rosenthal's (89) analysis of the normal vibrations of the pentatomic regular tetrahedron XY_4 to the determination of r_e(CH) for methane and find that r_e(CH) $= 1.080$ A corresponds to r_o(CH) $= 1.093$ A. This value of r_e is in reasonable agreement with a value of 1.077 A that can be obtained by a semiempirical method suggested by Myers & Gwinn (90). In this method the r_o(CH) and r_o(CD) of CH_4 and CD_4 are used to extrapolate r_o to infinite mass, i.e., to r_e.

Since rigorous or semirigorous evaluations of the relations between

[5] A step in this direction has been taken by Costain (118) for fluoroform.

r_e(CH) and r_o(CH) for the methyl derivatives are not available, it is of interest to examine what may be expected to be found if we employ a purely empirical guide. It has been found in the case of diatomic molecules that the equilibrium internuclear separation r_e and the corresponding vibrational frequency ω_e are related, for bonding between a particular pair of atoms, by an expression of the form $r_e \omega_e^n = $ constant. That is, a change in equilibrium distance is reflected as a change of opposite sense in the fundamental frequency. In order to provide a guide to the expected variation in r_e for the methyl compounds we tabulate $\nu(\parallel)$ and $\nu(\perp)$ for methane and for a number of its monosubstituted derivatives for which precise rotational constants, particularly A_o, have been determined, and also we tabulate the r_o(CH) deduced from the rotational constants (Table II). The complete absence of any correlation between the ν(avg.), the average CH stretching frequencies of the methyl group in these molecules, and the r_o strongly suggests that variations in r_o(CH) are a consequence of the neglect of the effects of the zero-point motion, and in fact that there exists little or no variation in r_e(CH) for this group of compounds.

Unusual Structures of Gaseous Molecules

The major source of information on the structures of gaseous molecules in recent years has been the rotational constants of various isotopic species of substances determined from microwave absorption spectra. As in the recent past this source of structural data has been supplemented by the determination of rotational constants from infrared rotation-vibration spectra and by electron diffraction studies. Molecules appear to have been chosen for investigation for reasons other than their particular interest to valence chemists. That is, they appear to have been selected because of the nature of the spectral interpretation problem they posed, rather than because of interest in the structure per se. However, examination of the list of compounds for which structural data have become available indicates that willy-nilly the results pose some interesting problems for valence theory to solve. In the following paragraphs we will indicate some of these problems.

As a first example we may consider the interatomic distances that have been reported for the two iso-electronic series ethylene, propylene, and isobutylene on the one hand, and formaldehyde, acetaldehyde, and acetone on the other. As has been pointed out elsewhere in this chapter, the CH distance in ethylene is less than it is in methane while in formaldehyde and acetaldehyde it is greater. McHugh & Schomaker (93) have reported the methyl CC distance in propylene (1.49 A) and isobutylene (1.50 A) to be between the typical single bond value 1.54 to 1.55 A and the short distance found in methyl acetylene and methyl cyanide (1.46 A) (80). The recent microwave work on acetaldehyde (91) has confirmed the prewar electron diffraction finding that the H_3CC distance in acetaldehyde is 1.50 A (94). In the case of acetone on the other hand, Allen et al. (95) report the carbon-carbon distance to be 1.55 A. The complete anomaly this long CC distance in acetone presents is particularly well demonstrated in Table III where there are compared related electronic properties of the two series of iso-electronic sub-

stances. The heats of hydrogenation, ionization potentials, and locations of the $N \rightarrow V$ transition all indicate that the CC distance in acetone should be less than 1.54 A.[6]

TABLE III

PROPERTIES OF ISO-ELECTRONIC $R_1R_2C{=}M$

	r(CH)		r(H₃C—C)		ΔH(ev)[*]		λ($N\rightarrow V$)[†]		I^z[‡]	
	M·CH₂	O	CH₂	O	CH₂	O	CH₂	O	CH₂	O
H₂C=M	1.070	1.12	—	—	−1.42	−0.89	1625	?	10.52	10.87
(CH₃)HC=M	—	1.114	1.49	1.50	−1.29	−0.70	1725	<1880	9.73	10.21
(CH₃)₂C=M	—	—	1.50	1.55	−1.22	−0.62	1845	1940	9.35	9.69

* Heats of hydrogenation in ev/molecule.

† Wavelength of $N \rightarrow V$ transition, A.

‡ Ionization potentials, ev/molecule, primarily from the photoionization method (96).

A second anomaly is to be found in the structure of sulfuryl fluoride. Lide, Mann & Fristrom (97) have investigated the microwave spectrum of SO_2F_2 and this work has eliminated most of the previously (98) reported discrepancies between microwave and electron diffraction (99) structure determinations. One point of discrepancy remains, namely the SO distance. Lide *et al.* (97) find 1.405 A for this distance, significantly shorter than the electron diffraction value 1.43 A which is also found in sulfur dioxide (100, 101) and sulfur trioxide (102). The difficulties encountered in explaining why the SO distance in the oxides is less than the double bond value (1.48 A) (103) are increased if the sulfuryl fluoride value is 1.405 ± 0.003 A.

The structure determination by Smith & Hedberg (104) of dinitrogen tetroxide presents the problem of explaining the coexistence of a very long distance and a high barrier to rotation. The nitrogen-nitrogen distance for the gaseous molecule is found to be 1.75 A (104), 0.27 A greater than twice the nitrogen atom single bond radius (0.74 A) (103). Snyder & Hisatsune (105) report the barrier restricting rotation about this NN bond to be 2.9 kcals./mole. Similarly, long X—NO distances have previously been reported in nitrosyl fluoride (106), chloride and bromide (107).

Four papers have appeared which contain structural information on substituted silanes. Newman *et al.* (108) combine infrared measurements with earlier microwave data on silyl fluoride, chloride, and bromide to conclude that the SiH distance in these three molecules is 1.477 ± 0.003 A as in silane (109) and methyl silane (120). Laurie (110) reports on the structure of SiH_2F_2, thus completing the series of fluorosilanes, and finds within his estimates of uncertainties the SiH distance to be the same as in SiH_3F and $SiHF_3$. Thus, it would appear that the silicon-hydrogen distance in the vari-

[6] The argument that 1.55 A for the CC distance in acetone is too long finds support in the preliminary structure found from the microwave spectra of acetone and acetone-d_6 by Swalen (119). He reports $CC = 1.511 \pm 0.005$ A on the basis of the reasonable assumption that $CO = 1.216$ A.

ous halogen derivatives of silane behaves quite differently from the carbon-hydrogen distance in like derivatives of methane (81). In contrast to the different behaviors of CH and SiH in compounds $CH_{4-n}X_n$ and $SiH_{4-n}X_n$, Laurie (110) notes that the SiF distance shows the same type of systematic decrease with n as has previously been found for the CF distance in the fluoromethanes (81), the CCl in chloromethanes (81), and the NCl in methylchloroamines (111). Further, in contrast to the behavior of the fluoromethanes, the dipole moments of the silyl fluorides show a completely additive character (110).

Finally, as an example of how some anomalies perhaps enter the literature we point to the microwave determination of the structure of formic acid by Lerner, Dailey & Friend (112). They find a C—O bond distance of 1.312 ± 0.002 A which may be compared with the electron diffraction determinations of the distance of 1.368 ± 0.034 A (113) and 1.36 ± 0.01 A (114). The other features of the structure as found in the microwave determination are in reasonable agreement with the electron diffraction results. Although it is not obvious, a choice has to be made in microwave determinations of this type, where no oxygen isotopic substitutions are employed, between two sets of oxygen positions which fit the data equally well. This situation arises because only the squares of the oxygen parameters are determined. In the present case the other choice of oxygen positions leads to a C—O distance of 1.358 A, but to a C=O distance of only 1.187 A which may be compared with the value of 1.245 ± 0.002 A which was chosen and to the electron diffraction values of 1.213 ± 0.026 (113) and 1.23 ± 0.01 A (114). Also this second set of oxygen positions leads to an OH distance of 0.87 A as compared to the value 0.95 ± 0.02 A obtained from the first set. The point then is that regardless of which set of oxygen positions is chosen there is disagreement between the microwave determination on the one hand and the electron diffraction determinations on the other. It is difficult to understand how two independent electron diffraction studies could have been in error by some 0.05 A in the determination of a CO distance in a molecule as simple as HCOOH. It is, of course, possible that the microwave results are correct, but it would seem that in view of the earlier electron diffraction work the burden of proof was on the microwave work and that the greatest care should have been taken in the interpretation of the data. Nevertheless, in the microwave study the assumptions were made that the molecule is planar and that substitution of deuterium for hydrogen has no effect on the structure. These assumptions, though possibly necessary, are surely not strictly valid in view of the nonrigidity of the molecule. At the very least, a justification of the assumptions is needed before the microwave determination can be considered reliable, particularly to the stated limits of error. Ideally, such a justification, if it is possible to obtain, should be based on a normal coordinate treatment of the internal motions of the formic acid molecule.

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STATISTICAL MECHANICS[1]

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Statistical mechanics aims at the interpretation of the observed or macro-. scopic properties of matter in bulk in terms of the mechanical properties of the constituent molecules and their interaction. It is an obvious principle of statistical mechanics that a complete knowledge of the properties of individual molecules and their interactions is sufficient for the prediction of the observed properties of bulk matter. If the molecules, i.e. the repetitious units, are sufficiently simple, a good deal of progress has been made toward actually accomplishing these possibilities.

The field of statistical mechanics may conveniently be considered to consist of two parts, equilibrium and nonequilibrium statistical mechanics. The first part deals with the thermodynamic properties of systems in equilibrium. The second part deals with the transport properties and the approach to equilibrium in nonequilibrium systems.

Van Hove (1) has recently given an interesting review of the general problems and aims of statistical mechanics. This rather brief survey discusses both equilibrium and nonequilibrium statistical mechanics and, in particular, points out some of the fascinating problems which remain unsolved.

EQUILIBRIUM STATISTICAL MECHANICS

It is well known that all the thermodynamic properties of a system may be written in terms of the partition function. The problem is, thus, that of evaluating the partition function for the various systems of interest. This situation is to be contrasted with that of nonequilibrium statistical mechanics in which some of the formal problems associated with the approach of systems to equilibrium remain unsolved. The simplicity of the expressions for the partition function, however, is somewhat misleading. Difficulties arise in that some of the interesting properties of the system, including in particular the condensation phenomena, manifest themselves only when the system has a large number of degrees of freedom, i.e., contains a large number of particles. In most cases, it is necessary to consider the limit in which $N \to \infty$.

The statistical mechanics of systems in equilibrium has recently been discussed in the comprehensive book by Munster (2). The first part of this book is devoted to a discussion of the basis of statistical mechanics. The

succeeding three parts are devoted to discussions of the theories of gases, crystals, and liquids.

The thermodynamic properties of dense gases and liquids may easily be expressed in terms of the properties of a perfect gas and correction terms which depend on the equation of state. The properties of the perfect gas depend only on the properties of the individual molecules, whereas the equation of state depends primarily on the nature of the interaction between the molecules.

The thermodynamic properties of perfect gases made up of simple molecules may, of course, be easily evaluated. The evaluation of the partition function of some of the more complex molecules, however, has not yet been accomplished. The contribution of the internal rotation to the partition function of methanol and similar molecules has recently been discussed by Halford (3).

On the other hand, there are many interesting problems associated with the equation of state of both dilute gases and dense gases and liquids. The basic problem is the quantitative dependence of the equation of state on the intermolecular potential. In addition there are interesting qualitative questions concerning the nature of condensation and the critical point, and the influence of quantum mechanics.

Dilute gases.—Various methods have been used to obtain density (or virial) expansions of the equation of state and other equilibrium properties. Perhaps the best known of these are the related cluster methods of Mayer and others (4) and Kahn (5). In these methods the thermodynamic functions and the distribution functions are expanded in powers of the activity. The density expansions are then obtained by first inverting the series for the density or first distribution function. Another method of obtaining such density expansions has been developed by Bogolyubov (6). He derived a set of coupled differential equations, from the Liouville equation, for the derivatives with respect to the coordinates of the coefficients in the density expansions of the distribution functions. Bogolyubov then solved these equations using an assumed "product condition." Both of these methods are limited, in general, to large systems and the results apply strictly only in the limit as $N \to \infty$. It has often been pointed out [see in particular, Yang & Lee (7)] that in the study of condensation, care must be taken in considering the limit, $N \to \infty$.

In an interesting new treatment of this problem, Oppenheim & Mazur (8) and Oppenheim (9) have obtained density expansions of distribution functions of finite systems. They derived a set of integrodifferential equations involving derivatives with respect to the volume, or density, using the scale factor method and an assumption of short, finite range pair interactions. The λth coefficient in the density expansion was obtained as a polynomial of degree λ in $1/N$, where N is the number of particles. These results are of interest in problems dealing with fluctuations and in the study of condensation phenomena. In particular, they may add to the understanding of the

manner in which the equation of state varies as one approaches the limit, $N \to \infty$.

Let us now return to the well-known expressions for the virial coefficients of the equation of state of an infinite system. Numerical values of the second virial coefficient for many forms of the potential and values of the third virial coefficient for a few potentials have been available for some time. Recently, a general method of evaluating the third virial coefficient for any intermolecular potential in which the interaction varies as the sum of inverse powers of the distance outside a hard sphere core has been described by Alder & Pople (10). The method is based on an expansion of the Boltzmann factors, $\exp(-\phi/kT)$, (ϕ is the intermolecular potential) in regions in which the potential is finite. This reduced the problem to that of evaluating integrals of negative powers of the separation distances. Alder and Pople have evaluated these integrals both analytically and numerically. The evaluation of a third virial coefficient for such a model then involves only algebraic operations using the tabulated functions. The method can be extended to angular dependent potentials, quantum effects, and mixtures.

Dense gases and liquids.—The theories of the equation of state of dense gases and liquids have for the most part been either modifications of the "cell" or "lattice" theories in which the effect of holes (empty cells) or multiple occupancy of the cells is taken into account, or they have been based on an approximate evaluation of the radial distribution function. A comprehensive discussion of the properties of liquid mixtures or solutions has recently been given by Prigogine (11). Although the emphasis of this book is on the properties of mixtures, it necessarily includes a detailed discussion of the theories of pure liquids.

The cell theories of the liquid state are based primarily on the early treatment of Lennard-Jones & Devonshire (12). In this treatment, they introduced the idea of a regular lattice with associated cells and one particle in each cell. The approximation was then introduced in which each particle was pictured as moving in its cell in the average field of force of the neighboring particles. This approach neglects all correlation effects and all effects associated with the interchange of particles among cells (communal entropy). It is, of course, clear that this treatment gives considerably too much local order to the liquids. In a series of early papers, Eyring and co-workers (13) made a good deal of progress in correlating various properties of liquids on the basis of similar theories associated with a lattice concept. These papers introduced the important idea of vacant lattice sites, and it was assumed that these vacant cells or holes played an important role in the behavior of liquids particularly near the critical point.

De Boer (14) has recently presented a generalization of these cell methods. In this treatment, he used a cell lattice with one cell for each particle and took into account in a systematic manner the collective motion in cell-clusters of the corresponding number of particles. In this manner he developed a rigorous expression for the partition function of the system in

terms of cell-cluster integrals over clusters of two, three, . . . , cells. These expressions involve a complicated combinatorial factor which has been considered by Cohen, de Boer & Salzburg (15). Their treatment of the one-dimensional case is exact, and they obtained approximate solutions for the two- and three-dimensional cases. The latter authors later (16) applied the results of the cell-cluster theory to a gas in which the total intermolecular potential field could be approximated by an harmonic potential field. This approach gave an improvement of the single cell (Einstein) theory. The first cell-cluster approximation in itself gave about half of the entropy difference between the single cell theory and the exact result. A fourth paper in the series, by Salzburg *et al.* (17) applied the cell-cluster theory to a liquid made up of hard spheres. The corrections introduced by considering cell-clusters of two cells were investigated using both a simple cubic and a face centered cubic lattice. The double cell partition function was calculated in an approximate manner. The results were compared with the Monte Carlo calculations of Rosenbluth & Rosenbluth (18).

Other modifications of the cell theories have involved the introduction of holes, i.e., vacant sites in the basic lattice. Various modifications of the hole theories of Cernuschi & Eyring (13) and Ono (19) have been discussed by Rowlinson & Curtiss (20).

The "lattice gas" as an idealization of the hole theories of liquids has been the subject of a good deal of study. A lattice gas is a system in which particles and vacancies are distributed in a regular array of lattice sites, and usually only interactions between neighboring lattice sites are considered. A new approach to the equation of state of a lattice gas has recently been given by Levine, Mayer & Aroeste (21). They obtained an expression for p/kT as a power series in the interaction parameter with coefficients being functions of the activity. They applied the result in some detail to the cubic close packed lattice. For this lattice they also obtained expressions for the probability of finding a cell adjacent to a filled cell also filled. The method is of interest both because it may readily be extended to include the effect of interactions between next nearest neighbors and higher interactions and because the method may be extended to a continuous coordinate space. Levine (22) has extended the study of the lattice gas to multicomponent mixtures. He obtained an expression for p/kT, for an arbitrary lattice, as a multiple power series in a set of interaction parameters depending upon the species and the separation distance in the lattice.

Levine, Mayer & Aroeste (23) have also used some of the results of the study of the lattice gas in a modification of the cell theory of Mayer & Careri (24). The treatment of Mayer & Careri is based on the use of a synthetic distribution function which permits both empty and occupied cells and the use of a Gaussian probability distribution for the location of any molecule in its cell. The more recent treatment is based on the use of a distribution function which contains, in addition, a parameter which correlates the probability of a distribution with the number of pairs of particles in adjacent cells.

As in the original treatment, Levine, Mayer & Aroeste also used a variable mean number of particles per cell, a variable cell size, and a variable distribution of particles with respect to the cell centers. The energy was approximated by the sum of interactions between nearest neighbors only, and the parameters of the distribution function were chosen so as to minimize the Helmholtz free energy. In this manner, they obtained a numerical equation of state for gases in the neighborhood of the critical point. In addition they made an estimate of the improvement which might be expected from the inclusion of the interaction between next nearest neighbors.

Cohen (25) has recently discussed the cell theories of the liquid state in considerable detail, and has extended the cell cluster theory of de Boer and collaborators to mixtures. He also discussed the introduction of holes into the cell-cluster theory as a special case of the binary mixture theory. The application of the results to a one-dimensional gas indicated a considerable improvement of the calculated entropy over the results obtained from cell-cluster theory without holes.

Some interesting new results on the equation of state of multicomponent mixtures have recently been obtained by Salzburg, Wojtowicz & Kirkwood (26). They have reduced the configurational partition function of a multicomponent mixture to the form of that of a single component with an intermolecular potential which is a function of the actual potentials, the composition and the temperature. The treatment does not depend upon the existence of any lattice structure or any other model. In addition, they developed two approximations to the rigorous theory that may be used as the basis of numerical calculations. These approximations are based on a method of moments, which was used previously by Kirkwood, and a generalization of this method, which makes use of an approximate evaluation of the pair distribution function. In the lowest approximation of the method of moments, the effective potential is a sum of pseudo pair potentials which, in turn, are quadratic functions, in the mole fractions, of the true intermolecular potentials. In a later paper, Wojtowicz, Salzburg & Kirkwood (27) used these results in a study of the theoretical basis of the theorem of corresponding states for mixtures.

The equation of state of liquids may also be expressed simply in terms of the radial distribution function. The evaluation of the radial distribution function has recently been discussed by Poirier (28). This treatment is based on an expansion of the distribution function of a partially coupled subset of particles of the system as a multiple Taylor's series in the coupling parameters. Poirier then solved the resulting set of linear integral equations by means of an approximation which is less drastic than the superposition approximation.

Wood & Parker (29) have recently used the Monte Carlo method to compute an isotherm for a system made up of molecules which interact according to the Lennard-Jones potential. The Monte Carlo method is a numerical method based on the theory of Markov chains. The isotherm is at a reduced

temperature of $kT/\epsilon = 2.74$ and for molar volumes between 0.75 and 7.5 times $N\sigma^3/\sqrt{2}$. It is of interest that the results indicate a liquid-solid transition; the properties of the transition have not yet, however, been well determined. The comparisons made by Wood and Parker indicate that the numerical isotherm is in essential agreement with the experimental results of Michels. A comparison with the simple Lennard-Jones Devonshire cell theory seems to indicate that the cell theory is surprisingly correct in the solid region but fails in the liquid region. On the other hand a comparison with the Kirkwood-Born-Green results based on the superposition approximation indicated good agreement at least at the lower volumes.

Two phase systems.—Although the questions concerning the quantitative equations of state of liquids and dense gases discussed above still present unsolved problems, even more fascinating problems are associated with the discontinuous phase transitions between these two states. Although it is surely to be expected that these condensation phenomena may be explained in terms of the qualitative nature of intermolecular forces, considerable effort has been expended to show that the exact statistical mechanical formulation of the equation of state leads to the existence of gas-liquid and liquid-solid phase transitions.

Some time ago, Onsager (30) in his study of the two-dimensional Ising model of ferromagnetism and later Yang & Lee (7) in their study of the related model of the lattice gas found condensation phenomena with critical temperatures. Condensation phenomena in a lattice gas have recently been studied by Morita (31, 32) using a generalization of the "cluster variation method" of Kikuchi (33) and Kurata, Kikuchi & Watari (34). In this treatment, the effect of particles at neighboring lattice sites on the probability of occupation of a particular site is taken into account in the Bethe approximation. The results indicate not only a gas-liquid transition with a critical point but also liquid-solid and gas-solid transitions. Furthermore, the calculated phase diagram is in reasonable agreement with the experimental diagram for argon. It would appear, therefore, that a complete statistical mechanical formulation would yield the complete equation of state, since none of the simplifying features of the lattice gas approximation would be expected to affect these results, qualitatively. In another approach to the problem, which is due principally to Mayer (35) the condensation phenomena are associated with singularities in the series expressions for the pressure and the density in terms of the activity (32).

Additional interesting problems arise when one considers the kinetics of the phase changes. These problems of the time lag in nucleation have recently been discussed by Frisch (36).

A complete theoretical treatment of two phase systems must, of course, consider the interfacial region and the nature of surface tension. In a series of three papers, Buff (37) and Buff & Saltsburg (38, 39) have considered the properties of curved fluid interfaces. In the first paper the effects of the presence of external fields were examined from a molecular point of view.

In particular, this paper was concerned primarily with the verification of a generalized Gibbs-Kelvin formula, which implies the partial differential equation determining the shapes of interfaces subjected to geometrical constraints. The second paper discussed the confluence properties of three fluid phases and led to a generalization of the Neuman surface tension triangle, which provides the boundary conditions on the equations describing the surfaces of fluid lens. It was found that the classical equation must be supplemented by a thermodynamic length parameter. The third paper of the series discussed the dependence of the free energy on the parameters of external force.

Quantum effects.—The studies of the equilibrium properties of gases and liquids discussed, thus far, have been primarily restricted to those conditions under which classical mechanics provides an adequate description of the system. To a good approximation quantum effects may be considered to be of two types: (a) diffraction effects, which result from the wave nature of the molecules (or the quantization of the interaction between the molecules) and which are important when the de Broglie wavelength associated with the molecules is of the order of magnitude of the molecular diameter; and (b) symmetry effects, which result from the statistics of the particles (the restriction to wave functions of the proper symmetry), and which are important when the de Broglie wavelength is of the order of magnitude of the average distance between the molecules.

The temperature dependence of the molecular distribution functions including quantum effects has been considered by Oppenheim & Ross (40). The treatment is based on a derivation from the Bloch differential equation of an integrodifferential equation for the temperature dependence of the Wigner distribution function of a canonical ensemble. Oppenheim & Ross solved the resulting equation by two series methods. The first is a series in powers of Planck's constant and hence is useful in the study of nearly classical systems. The second method is a perturbation method in the intermolecular potential.

It is well known that the symmetry effects in a perfect Bose-Einstein gas, lead to condensation phenomena, similar to (but not identical with) the simple gas-liquid transition. The effect of a gravitational field on the thermodynamic properties of an ideal Bose-Einstein gas has been discussed by Gersch (41). He found that the gravitational field causes a jump discontinuity in the heat capacity at constant volume. Particularly, because of the similarity of this ideal Bose-Einstein condensation with the lambda point transition in liquid helium, a good deal of effort has gone into the study of the imperfect Bose-Einstein gas.

In a series of papers, Yang and others have discussed the properties of a Bose-Einstein gas made up of hard spheres. Huang & Yang (42) first discussed the two-body hard sphere problem using a generalization of Fermi's pseudopotential. The boundary conditions on the problem of the interaction of two hard spheres were eliminated by the use of the pseudopotential and

the problem was formulated in terms of the phase shifts. They then showed that a pseudopotential can be used in place of the boundary conditions in the N-body problem. This led to an expansion of the energy levels of the system in powers of the hard sphere diameter. For the Bose-Einstein system, the first order energy expression exhibited an "energy gap" above the ground state, leading to properties of the system similar to that of a superfluid. Huang, Yang & Luttinger (43) then used the method of the pseudopotential to obtain expansions for the virial coefficients of an imperfect Bose-Einstein gas, in powers of a/λ where a is the rigid sphere diameter and λ is the thermal wave length $(2\pi\hbar^2/mkT)^{1/2}$. They obtained expressions correct to the order of $(a/\lambda)^2$. Huang, Yang, & Luttinger then considered a fictitious system with exactly the energy levels given by the first approximation, of Huang and Yang, discussed above. The partition function for such a system was calculated exactly and the exact equation of state was obtained. It was shown that such a system exhibits a phase transition, which more closely resembles an ordinary gas-liquid transition than the Bose-Einstein condensation. In a short note, Lee & Yang (44) then introduced a "binary collision" expansion method. This method which is applicable to an arbitrary interaction potential led to a systematic expansion of the quantum mechanical counterpart of the cluster integrals, b_l, in powers of a/λ. They then applied the method to Bose-Einstein, Fermi-Dirac, and Boltzmann gases made up of hard spheres. Explicit expressions were given for the fugacity expansions and other pertinent quantities. These results were discussed in more detail in a later paper by Lee, Huang & Yang (45), where the eigenfunctions and eigenvalues of a Bose-Einstein gas of hard spheres were again considered. The previous methods were shown to lead to expansions of the various quantities in powers of $(\rho a^3)^{1/2}$, where a is the hard sphere diameter and ρ is the particle density. They also obtained an expression for the pair distribution function in the ground state. This led to the definition of a "correlation length" which characterized the spatial extension of the correlation introduced by the hard sphere interaction.

Brueckner & Sawasa (46, 47) have also discussed the properties of an imperfect Bose-Einstein gas. They first considered the properties at low temperatures of a gas made up of molecules which interact according to an arbitrary repulsive potential. They pointed out that a principal difficulty which arises in any simple theory is that a perturbation evaluation of the interaction energy leads to divergent results. They showed that this divergence is closely related to the large excitation energy required to remove particles from the ground state, i.e. to the existence of the "energy gap" in the spectrum. This difficulty was avoided by an exact method of dealing with that part of the Hamiltonian which gives rise to the perturbation divergence. The treatment of the region of large momentum transfers was carried out by introducing the concept of the "scattering length of interaction." In the following paper, Brueckner & Sawasa applied these methods to the study of a gas made up of hard spheres, and discussed the energy as a function of density from low density to the region of close packing.

The general problem of time-independent quantum mechanical perturbation theory applied to large systems has, also, been discussed recently by Tobocman (48) and by Hugenholtz (49). Hugenholtz considered only systems at or near the ground state, i.e., systems at very low temperatures. The latter treatment is based on a recent formulation of perturbation theory by Van Hove (50, 51), and an analysis of the volume dependence of the various contributions to the matrix elements.

Nonequilibrium Statistical Mechanics

Various interesting problems also remain in the study of nonequilibrium systems. It is well known that the dynamical equations of classical and quantum mechanics are reversible in time. Furthermore the dynamical states of any finite mechanical system undergo Poincare cycles. On the other hand, the macroscopic or thermodynamic behavior of a large system is such that the system approaches thermodynamic equilibrium. The origin of this "irreversibility" in the behavior of large systems has for a long time been one of the fascinating formal problems of statistical mechanics. These questions which are usually associated with the term "ergodic theory" have been discussed in some detail by Rosenfeld (52). A quantum mechanical proof of the recurrence theorem of Poincare, along with some comments on the statistical implications of the theorem, has recently been given by Bocchieri & Loinger (53). A proof of the ergodic theorem in quantum mechanics has also been discussed recently. The recent treatment of Ekstein (54) differs from the earlier treatment of von Neumann (55) in that it deals with a system immersed in a "temperature bath," rather than with an isolated system.

The conservation equations.—The thermodynamic or macroscopic state of a system in equilibrium is specified by a small number of "thermodynamic variables" associated with the time-independent integrals of the dynamical equations. For a simple single component system the integrals are: a constant, the total energy, and the components of the linear and angular momentum. For a system at rest, the first two integrals are associated with the density and the temperature and the remaining are zero. The macroscopic state of a nonequilibrium system is usually described by a specification of the thermodynamic variables as functions of position. The question of the adequacy and completeness of such a description of a system in a state not too far removed from equilibrium is discussed later.

The time variation of the macroscopic variables is described by the hydrodynamic equations of change or conservation equations. In their most elementary form these equations depend simply on the conservation principles of classical and quantum mechanics. The equations were derived sometime ago from the classical Liouville equation by Irving & Kirkwood (56) and using quantum mechanics by Irving & Zwanzig (57). Recently, Brittin (58) has considered in a similar manner a system of charged particles which interact only through the electromagnetic field. He treated the particles and fields statistically using both classical and quantum mechanics. Brittin found that the quantum statistical ensemble-averaged fields obey Maxwell's equations.

The form of the magnetohydrodynamic equations which he obtained, however, differ from those which have previously been considered to be exact.

The reciprocal relations.—In their most elementary form, the hydrodynamic equations involve various fluxes. In the case of a simple single component fluid, these are the fluxes of momentum and energy. The thermodynamics of irreversible processes is based on the assumption that for systems not too far removed from equilibrium these fluxes are linear functions of the "generalized forces." Many of the important results of this "phenomenological" treatment depend on the reciprocal relations of Onsager (59, 60).

A survey and discussion of the various derivations of the reciprocal relations along with a new derivation has recently been given by de Groot & Mazur (61). The previous derivations of the relations have been based on the study of fluctuations in systems at equilibrium. These approaches depend upon a hypothesis concerning the rate of regression of fluctuations. The treatment of de Groot & Mazur is based on the "master equation." The derivation of this equation, which depends upon statistical considerations of irreversible processes, is discussed in a later section.

The theory of the regression of fluctuations has been discussed by Fixman (62), from the point of view of "least-square prediction theory." This led to expressions for the transport coefficients in terms of correlations between the fluctuations and the time averaged fluxes. Fixman then developed dynamic approximations which make possible a computation of the transport coefficients. The approximations are analogous to those used in the cell theories of the equation of state. The theory of rate of regression of fluctuations has also been used by Kubo, Yokota & Nakajima (63) to obtain expressions for the transport coefficients. Their treatment is based on Onsager's (59, 60) assumption that on the average the regression of a spontaneous fluctuation follows the macroscopic laws.

Tisza & Manning (64) have considered the theory of fluctuations in the paths of approach of systems to equilibrium, i.e., time-dependent fluctuation theory as contrasted with the theory of fluctuations in equilibrium systems discussed above. The theory is based on a combined application of the phenomenological theory of dissipation and the stochastic theory of random processes. The use of the Langevin equation was replaced by the introduction of distribution functions over sets of fluctuation paths.

The transport equations.—The derivations of the conservation equations from the classical and quantum mechanical Liouville equations referred to above also led to expressions for the fluxes in terms of the molecular distribution functions. The problem of relating the nonequilibrium behavior of systems to molecular properties is thus reduced to that of determining the molecular distribution functions.

In a dilute gas the predominant contribution (and in the limit the only contribution) to the fluxes depends on the single particle distribution. The time variation of this single particle distribution function is described by the Boltzmann equation. This equation was originally derived in 1872 by Boltz-

mann (65) using purely geometrical arguments. In the last few years, considerable interest has arisen in the possibility of deriving this equation from the Liouville equation on the basis of statistical arguments. This interest is closely associated with the concept of "molecular chaos." As mentioned above, the purely dynamical equations, such as the Liouville equation, are reversible in time. The Boltzmann equation, however, is irreversible in time and all solutions apparently approach an equilibrium Maxwellian solution with increasing time. There is also the possibility of extending the range of applicability of the Boltzmann equation. The ordinary Boltzmann equation applies only to a dilute gas made up of spherical molecules under conditions such that classical mechanics is valid.

A quantum mechanical modification of the Boltzmann equation was first proposed by Uehling & Uhlenbeck (66). An equation quite similar to that of Uehling and Uhlenbeck has been derived by Saenz (67) for molecules of zero spin. The collision integral in this equation is expressed in terms of an exact cross section for binary collisions which takes into account the identity of the colliding molecules. In this derivation, Saenz used the properties of the Wigner distribution functions, Kirkwood's time-averaging procedures, and physical assumptions similar to those used by Ross & Kirkwood (68) in their derivation of the quantum mechanical Boltzmann equation. As is to be expected the equation derived by Saenz reduces to that of Ross and Kirkwood when one approximates the exact cross section by the first Born approximation.

A more general approach to the statistical mechanics of nonequilibrium systems is based on the "master equation." This equation, which is particularly well-adapted to quantum theory, describes the irreversible time evolution of the probability distribution function of the entire system. The equation was originally derived by Pauli (69) on the assumption that the phases (in the unperturbed wave function) are randomly distributed at all times. More recently, Van Hove (70) has derived the master equation to the lowest order in the perturbation using only the assumption of randomness of phases at the initial time and certain characteristic properties of the perturbation, which can be shown to hold for actual systems. Van Hove (71) has also extended the derivation to give a generalized master equation valid to arbitrary order in the perturbation. He then proved that the long-time behavior of the solution of the generalized master equation leads to the establishment of a microcanonical equilibrium with respect to the total Hamiltonian, including the perturbation.

Brout & Prigogine (72) have studied the classical form of the master equation. Using classical action and angle variables they considered irreversible processes in weakly coupled macroscopically homogeneous systems and obtained the master equation correct to the lowest order in the perturbation. Later Prigogine & Philippot (73) considered irreversible processes in nonuniform systems and the extent to which one may simply superimpose the flow terms on the collision terms. The derivation of the classical master

equation has been extended to an arbitrary order in the perturbation by Prigogine & Henin (74).

Brout (75) has also derived the master equation for a dilute macroscopically homogeneous gas from the classical Liouville equation. Kac (76) had previously shown that the master equation preserves in time the property of factorization of the higher order distribution functions into products of singlet distribution functions. This theorem then shows directly that the master equation is equivalent to the Boltzmann equation provided that the initial distribution function is factorable. The question as to whether the majority of initial ensembles are represented by factorable distribution functions remains unanswered.

The approach to equilibrium.—The rate of approach of systems to equilibrium has been the subject of several recent discussions. Montroll & Shuler (77) have carried out a theoretical study of the collisional and radiative relaxation of an interesting model consisting of a system of harmonic oscillators immersed in a "constant temperature heat bath." They obtained an exact solution of the relaxation equation for initial Boltzmann distributions, Poisson distributions, and delta-function distributions of the vibrational states.

The rate of approach to equilibrium in a system of charged particles in the approximation of two particle interactions resulting in small angle deflections has been studied by MacDonald, Rosenbluth & Chuck (78). The treatment was based on a Fokker-Planck equation derived by Rosenbluth, MacDonald & Judd (79). The relaxation of a distribution which was initially isotropic in the velocities and a delta function in the energy was studied using an electronic digital computer. The time required for the distribution to become Maxwellian throughout the range from zero energy to several times the average energy was found to be about ten times the "self-collision time" of Spitzer (80).

Transport coefficients.—An exact solution of the Boltzmann equation would give the singlet distribution function under nonequilibrium conditions, and then, along with the expressions mentioned above, would lead to general expressions for the fluxes. The Enskog series is supposed to represent such a solution. The convergence of the series and the uniqueness of the solution, however, has been the subject of considerable discussion. In particular, the Enskog solution leads to the curious paradox that a knowledge at an initial time of the density, stream velocity, and temperature, i.e., the first three moments of the distribution, at all points determines the entire distribution function at all later times. Grad (81) has discussed this question and has developed a more general series solution. Even the existence of spatially nonhomogeneous solutions of the Boltzmann equation, however, has been questioned by Morgenstern (82), and discussed recently by Laitone (83). Nevertheless, the expressions for the transport coefficients as based on the Enskog first approximation (the Navier-Stokes approximation) appear to agree well with experiment. These expressions give the transport coefficients

in a dilute gas made up of spherical molecules in terms of the intermolecular potential.

Recently, Mason (84) has derived expressions for the higher approximations (to the Navier-Stokes approximation) to the transport coefficients using both the method of Chapman & Cowling and a generalization of a method due to Kihara. In a second paper, Mason (85) has made extensive numerical computations of the corrections using both an inverse power repulsive potential and the more realistic "exp-six" potential. He considered, in particular, diffusion and thermal diffusion. The results indicate that the corrections for the higher approximations may often be rather large and for precise work the influence of these corrections may be significant.

Methods of obtaining information about intermolecular potentials and numerical values of the parameters have been discussed by Srivastava (86) and by Madan (87). Srivastava considered the interaction between the unlike pairs A-He, A-Xe, and Ne-Xe using the exp-six potential. Madan used the same potential along with data on the thermal conductivity and thermal diffusion to obtain an estimate of the parameters for krypton.

The effect of internal structure of molecules on the transport phenomena has been considered by Curtiss (88) and by Curtiss & Muckenfuss (89) by means of model in which the molecules were idealized as rigid nonspherical convex bodies. The treatment was based on a modification of the Boltzmann equation in which the rotational motion of the rigid ovaloids was considered from a classical point of view. This modified Boltzmann equation led to an equation of conservation of angular momentum in addition to the usual equations of continuity, motion, and energy balance. Associated with the additional equation one then has additional transport coefficients describing the transport of angular momentum. In the second paper the expressions for the transport coefficients were reduced to fourfold integrals over the surfaces of two ovaloids. Numerical values of the transport coefficients were obtained for the spherocylindrical model. The treatment has been extended to the diffusion coefficients and the transport coefficients of mixture of rigid ovaloids by Muckenfuss (90).

The kinetic theory of rigid ovaloids has also been considered by Kihara (91, 92). Kihara used a formal geometrical theorem to evaluate average cross-sections for collisions between heavy convex molecules and light spherical molecules. The dependence of the transport coefficients on the geometrical average cross-section which he then assumed may be shown to be an approximation to the more complete results mentioned above.

Hirschfelder (93) has considered the thermal conductivity of gases made up of polyatomic and electronically excited molecules. He derived a modified form of the Eucken expression for the coefficient of thermal conductivity. Further discussion indicated that metastable electronic species should have anomalously large coefficients of thermal conductivity, but that the usual excited electronic states should give smaller contributions to the coefficient of thermal conductivity than that predicted by the Eucken correction.

The rate of heat transfer in a chemically reacting mixture has also been considered by Hirschfelder (94). If the reaction rates are sufficiently fast the chemical composition at each point is very nearly that characteristic of local thermodynamic equilibrium. Under such conditions the heat transfer is similar to that through a single component with an effective coefficient of thermal conductivity. This problem has also been considered by Butler & Brokaw (95).

The problems of statistical mechanics are, thus, seen to be of many types. For example, there are the formal problems of ergodic theory and the derivation of the Boltzmann and master equations; there are the problems more directly related to experiment, such as the prediction of the equation of state and the transport coefficients; and there are the problems associated with the quantum effects at low temperatures. Finally, it should be mentioned that there are several additional interesting applications of statistical mechanics such as applications in the study of polymers and Brownian motion which have not been discussed in this review.

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HIGH PRESSURE DEVELOPMENTS[1]

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Introduction.—Because it seemed impractical to cover the entire field of high-pressure developments, the authors have limited the coverage to subjects of interest to them personally and to those subjects that seem to have significance for future developments. The field of high pressure, particularly at high temperature, has aroused a great deal of interest of late. Work which has not yet been published is under way in a number of laboratories.

The general effect of high pressure is one of closing up systems, thereby reducing their entropy. For example, a pressure of 12,000 atm. reduces the entropy of potassium metal by 30 per cent. Pressure in many respects, then, produces effects akin to low temperature (one cc. kiloatmosphere is equivalent to 12.19°K.). Thermodynamically, a system is completely characterized if the volume is known as a function of the two intensive properties, pressure and temperature, and if the specific heat at constant pressure is known as a function of temperature (the foregoing statement assumes that E_0 and S_0 are known). Of course if the foregoing thermodynamic quantities are known for the components of interest in a chemical reaction, the intensive quantities, pressure and temperature, could be adjusted to give favorable thermodynamics for the formation of the desired products. Considerable use of temperature has been made to bring about chemical and physical changes in systems since temperatures in the range of 500°C.–2000°C. readily supply energies equivalent to thos found in most chemical bonds. However, comparatively little use has been made of pressure because experimental techniques for producing pressures of the order of 100,000 atm. are extremely difficult (such pressures are required to provide compressive energies which correspond in magnitude to chemical bond energies).

In addition to thermodynamics, the chemist must be concerned with the problem of reaction rates when he desires to bring about a transformation. In general, experience indicates that low temperature is unfavorable for chemical reactions to proceed at a reasonable rate. Likewise high pressure generally reduces reaction rates considerably. For this reason it is desirable to be able to obtain high temperatures and high pressures simultaneously in order that reactions will proceed at a reasonable rate under high-pressure conditions. Many compounds which cannot be synthesized at atmospheric pressure due to instability can be produced with ease under high pressures.

[1] The survey of literature pertaining to this review was concluded December 7, 1958.

By cooling these compounds before releasing the pressure, many of them gain metastability of such an order that they show no tendency to revert. Detailed treatments of the foregoing considerations have been given by Hall (1, 2), Kistler (3) and Hall *et al.* (4).

High-pressure, high-temperature apparatus.—A major deterrent to the pursuit of experimental work at high pressure and high temperature has been the nonexistence of equipment capable of producing high temperature and pressure simultaneously. A brief review concerning such apparatus, therefore, seems appropriate. The first high-pressure, high-temperature apparatus of note was built by Parsons for his work on diamond synthesis (5). In this apparatus a refractory substance provided thermal and electrical insulation and also transmitted pressure from a moving piston to the specimen. The latter was heated by electrical resistance methods. Bridgman (6) and others have immersed high-pressure systems in a thermostatic bath, but heating accomplished by this method is limited to the neighborhood of 300°C. for systems constructed of steel.

A double-ended simple piston and cylinder apparatus utilizing internal electrical heating has been described by Coes (7). This apparatus is shown for the first time in an article by Roy and Tuttle (7a). In this apparatus the sample is enclosed in a metallic container that is in turn surrounded, first, by MgO powder and, second, by a graphite cylinder. This assembly is squeezed between two tungsten carbide pistons working in each end of a hot-pressed alumina cylinder. The sample is heated by a low-voltage current passing through the graphite. The alumina cylinder provides necessary electrical and thermal insulation. Although alumina possesses high strength in compression, its tensile strength is relatively low. Consequently the alumina cylinder is supported laterally by a press-fit, hardened steel binding ring. The pressure on the pistons is maintained by a hydraulic press. This apparatus can be used at pressures of 35,000 atm. at temperatures below 900°C. for sustained periods of time. Runs have been made at 45,000 atm. at lower temperatures by accepting a reduced life for the apparatus. The temperature of the sample in this apparatus cannot be determined very precisely. An approximate calibration of the pressures has been achieved by use of the bismuth I→II transition.

Butuzov, Gonikberg & Smirnov (8) have briefly described a high-temperature, high-pressure apparatus that has been used at pressures of 35,000 atm. and temperatures of 600°C. This apparatus is an adaptation for high temperature use of an apparatus originally designed by P. W. Bridgman. The material under study is contained in a small furnace wound with electrical resistance wire. Pressure is transmitted directly into the material in the furnace by a mixture of isopentane and *n*-pentane. An apparatus very similar to that of Butuzov *et al.*, except that the pressure-transmitting medium is an inert gas, has recently been described by Birch & Robertson (9). This apparatus has been used at pressures to 34,000 atm. at temperatures of 1000°C.

Griggs & Kennedy (10) have introduced a simple apparatus, based on the principle of Bridgman's anvil apparatus (11) which provides pressures of 80,000 atm. at 500°C., 50,000 atm. at 800°C. and 20,000 atm. at 1000°C. This apparatus, which is finding widespread use, has come to be known as the "simple squeezer." The specimen to be compressed is contained in a disk-shaped, metal box of inside dimensions approximately one-quarter inch diameter by .005 inches height. The anvils are made of either cemented carbides or Stellites. Heating is accomplished by surrounding the entire anvil assembly with a resistance-heated furnace. Pressure obtained between the anvils is taken as force per unit area on the anvil face. This device has two drawbacks: (*a*) There is some uncertainty as to the actual pressure transmitted to the specimen and (*b*) the sample space is very small. The small sample volume is inherent in the design and cannot be increased appreciably by scaling up the apparatus.

A simple piston and cylinder high-pressure, high-temperature device somewhat like that of Coes has been used at Brigham Young University (12). In this design, the specimen is contained in an electrically conducting tube that may be heated by an electrical current. Pressure is transmitted to the sample by a fine-grained refractory solid such as pyrophyllite.[2] This material also serves as thermal and electrical insulation. Pressure generated within the sample tube is determined from a calibration plot that is constructed from measuring the load required to obtain known electrical resistance discontinuities in Bi and Tl [Bridgman has discovered sharp changes in electrical resistance occurring in Bi at 24,800 atm., Tl at 43,500 atm., Cs at 53,200 atm., and Ba at 77,400 atm. (13)]. These transitions serve as very useful reference points for pressure calibrations. This apparatus is satisfactory for use at maximum pressures of 50,000 atm. at temperatures of 5,000°C. The higher temperatures are obtained when graphite is used as the sample tube. The use of a refractory medium for transmitting the pressure to the sample is, of course, a return to a method (already mentioned) used by Sir Charles Parsons in 1888. This seems to be the only satisfactory solution to the problem of generating extremely high pressures at extremely high temperatures. Although there is frictional hold-up within the refractory medium, it is reproducible, easy to measure and to make allowances for.

The problem of generating pressures above 50,000 atm. is difficult. The main limitation is one imposed by the strength of materials that might be used for constructing the high-pressure apparatus. Cemented tungsten carbides, the most satisfactory material presently available, has a compres-

[2] This material, a hydrous aluminum silicate, is a naturally occurring substance. In the United States it is mined in the southeast and is available from the American Lava Company, Chattanooga 5, Tennessee, as "Grade A Lava." *Catlinite* or "Pipestone" a material often used by Bridgman is very similar to *pyrophyllite*, differing mainly in that it contains Fe_2O_3. "Soapstone" or *talc* is similar to pyrophyllite, being a hydrous magnesium silicate. All these materials have been utilized in high pressure gasketing applications for many years.

sive strength of the order of 50,000 atm. maximum. One of the most satis-
factory ways to make this material serviceable at pressures beyond its normal
compressive strength is the use of a principle, first recognized by Bridgman,
known as the principle of massive support. This is the principle at work in
anvil apparatus. Bridgman's anvil apparatus is primarily a two-dimensional
device in which the sample to be compressed has appreciable breadth and
width but very small depth and, consequently, a small volume. It would be
very desirable somehow to preserve in a three-dimensional device the fea-
tures that make this two-dimensional device operable. In a practical three-
dimensional device it would be desirable to have the breadth, width, and
depth of the sample of comparable dimensions. The salient features of
Bridgman's anvil apparatus have been utilized by Hall in the construction
of a three-dimensional device called the *tetrahedral anvil apparatus* (12). At
this writing this apparatus has been successfully used at pressures of
100,000 atm. and temperatures of 3,000°C. Instead of two opposing anvils
with circular faces, four anvils with triangular faces have been used in this
equipment. The four anvils are driven together by hydraulic rams along lines
normal to the triangular faces, said lines intersecting at tetrahedral angles
in the center of a regular tetrahedral volume enclosed by the anvils them-
selves. In this device, a regular pyrophyllite tetrahedron, the edges of which
are 25 per cent longer than the corresponding legs on the triangular anvil
faces, serves as pressure-transmitting medium, thermal and electrical insula-
tion, and, by extruding between the anvils as they advance, provides the
necessary compressible gasket. The sample container, a tube which also
serves as electrical resistance heater, is located within the pyrophyllite tetra-
hedron and runs diagonally from opposite edges. Electrical connections are
made to the sample tube through metal tabs which make contact with the
anvils. A thermocouple is spot-welded or inserted in the wall of the sample
container, and the leads are brought out through edges of the pyrophyllite
tetrahedron. Friction of the pyrophyllite on the thermocouple leads is suf-
ficient to hold them in place during high-pressure operation. Pressure trans-
mitted to the contents of the sample tube is measured by noting changes in
electrical resistance of Bi, Tl, Cs, and Ba.

A two-stage apparatus for measuring volume as a function of pressure to
100,000 atm. at room temperature has been described by Bridgman (14). A
stepped-piston apparatus capable of developing maximum pressures near
200,000 atm. in which P-V relationships may be measured at room tem-
perature has been developed at Brigham Young University (12).

Jamieson (15) has described a technique whereby x-ray diffraction studies
may be made of substances at pressures in the neighborhood of 24,000 atm.
In his device the pressure vessel is a three-carat single crystal diamond
through which a highly polished straight hole .015 inch in diameter and .172
inch in length has been ground. Pistons, which are driven into each end of
the hole by a calibrated spring, are air-hardened drill rod .090 inch long.

A similar device has been built at the U. S. Bureau of Standards. The diamond they utilized is a large stone confiscated by the U. S. Customs.

A modified form of Bridgman's anvil apparatus has been devised by Chester & Jones (16) for making superconductivity measurements at low temperature. Ferro-magnetic materials complicate superconductivity measurements; therefore beryllium copper was used as the material of construction.

Fitch, Slykhouse & Drickamer (16a), at the Department of Chemistry, University of Illinois, have devised an apparatus for measuring the optical properties of solids at pressures as high as 200,000 atm. This apparatus uses an alkali halide (normally sodium chloride) as a pressure-transmitting medium. Sodium chloride windows are used in this apparatus. The salt is fused in a long narrow hole that extends into the region of high pressure. The rate of extrusion of the sodium chloride at the extreme pressures used is sufficiently slow that optical measurements can be made. The specimen on which measurements are to be made is a thin wafer. It is squeezed between anvils which employ Bridgman's massive support principle. In addition, however, another principle is employed: the anvil is tapered on the sides, i.e., the anvil is a truncated cone. Sodium chloride surrounds this tapered region. When pressure is applied a pressure gradient exists along the taper. This pressure gradient gives a "multi-staging" effect and consequently allows a greater pressure to be sustained between the anvil faces. The greater the taper, the higher the gradient, but also the higher the tendency for compressed material to extrude from between the flat anvil faces. Fitch, Slykhouse & Drickamer have found that a single taper of six degrees on each side of the piston was the most advantageous.

The design of high-pressure, high-temperature apparatus for use in the 100,000 to 1,000,000 atmosphere range is an extremely important problem. The upper limit of pressure usefulness of any device is determined by the compressive strength of the materials of construction. A direct approach to the problem of obtaining higher pressures, then, is to be found in the field of materials. Diamond has the highest compressive strength of any known substance (about three times that of cemented tungsten carbides). Its extremely high cost and unavailability in large sections precludes its general use in high-pressure equipment. Diamond powder, however, is available in sufficient quantity and at such a price that a cemented diamond composition analogous to the cemented carbides could be used if such were obtainable. Although nothing has been published concerning such compositions, it is known that some work is being conducted in this area.

Melting point effects.—The study of melting point phenomena under high pressure conditions (particularly above 100,000 atm.) should eventually shed some light on the old question as to the character of the melting curve as pressure is increased indefinitely. Undoubtedly such studies will improve our comprehension of the nature of liquids and solids and the phenomena of

melting. Pressure can either increase or decrease a melting point. If the liquid is more dense than the solid, application of pressure will lower the melting point. Conversely, if the solid is more dense than the liquid, the melting point will be raised. For pressures of the order of 100,000 atmospheres the change of melting temperature may be several hundred degrees C. Butuzov, Boksha & Gonikberg (17), utilizing apparatus previously referred to, have measured the melting point of black phosphorus and have found that the melting point rises smoothly with increasing pressure to about 1000°C. at 18,000 atm.

Butuzov & Ponyatovskiĭ (18) find that the mean increase in the melting point of In under pressure is 4.13×10^{-3} degrees per kg./sq. cm. over the range 0 to 3×10^4 kg./sq. cm. (1 kg./sq. cm. = .968 atm.). The change in melting point is almost linear. The Clapeyron equation gives the change in volume of In on melting as 2.93×10^{-3} cc./gm. No polymorphic changes were detected.

Butuzov & Ponyatovskiĭ (19) investigated the phase diagram of bismuth at pressures to 30,000 kg./sq. cm. at temperatures between the melting point and room temperature. The β phase melts in the pressure range of 17,300 to 22,400 kg./sq. cm. at a constant temperature of 184°C. and hence becomes liquid without change in volume. The melting point of the γ phase increases 0.0072° per kg./sq. cm. The phase changes $\alpha = \beta$ and $\beta = \alpha$ take place very rapidly and with marked hysteresis in the temperature range studied (rate of change of temperature approximately 1°/sec.). At 20° the hysteresis in terms of pressure is approximately 1000 kg./sq. cm. for the $\alpha = \beta$ transition and approximately 900 kg./sq. cm. for the $\beta = \gamma$ transition. Butuzov & Gonikberg et al. (8) report the change in melting point of bismuth as a function of pressure to 22,000 kg./sq. cm. The melting point decreases regularly from 270° at one atm. to 187° at 18,700 kg./sq. cm.

Butuzov & Gonikberg (20) have measured the melting temperature of Sn and Pb at a maximum pressure of 33,000 atm. At this pressure the melting point of Sn has increased to 315°C. and that of Pb to 527°C. In both cases no new phases are encountered and the melting curve is a smooth function.

Hall (21) has reported the melting point of Ge as a function of pressure to 180,000 atm. The melting point decreases linearly from 936° at one atm. with a slope of -3.27×10^{-2} degrees per atm. The linear dependence indicates that no new solid phases form over this pressure range and that the liquid remains the more dense phase. Electrical resistance measurements indicate that the solid remains a semiconductor and the liquid displays metallic conduction over the entire pressure range.

As yet unpublished is some work by Dr. S. P. Clark (21a) of the Geophysical Laboratory, Carnegie Institution of Washington, on the melting points of NaCl, NaBr, NaI and KCl to 25,000 atm. The apparatus used is that of Birch's as previously described. Clark reports the melting point of NaCl increases from 800° to approximately 1150° at 25,000 atm.

Some recent theoretical work concerning melting points at high pressures

that may be of interest are those of Valles (22), where the melting point of Fe at 4×10^7 atm. has been estimated to be 8136°C., and Gilvarry (23), where fusion curves for the alkali elements have been predicted for high pressures. The question as to the existence of a critical point between liquid and solid at high pressures has been considered from a theoretical standpoint by Ebert (24) and by Zernike (25).

Of considerable significance to high-pressure work, when a fine-grained refractory material is used to serve as the thermally insulating container and also as pressure-transmitting medium, is the fact that extreme pressure can increase a refractory's melting point by several thousand degrees. Thus, with such a system, it is possible to operate under high pressure conditions at higher temperatures than is possible with the same materials at one atm.

Diamonds.—Since the motivating force behind the development of high-pressure, high-temperature techniques over a period of 100 years or so has been the desire to produce man-made diamonds, it seems appropriate to include in this review something concerning this subject. Perhaps the most cogent remark that can be made concerning the present status of man-made diamonds is that the Metallurgical Products Department of the General Electric Company, Detroit, Michigan, is now displaying pictures of a pretty girl with an "ohhh, diamonds!" expression looking at $30,000 worth of synthetic diamond grit. No direct statements or publications have been issued describing the details of work carried out at the General Electric Laboratory at Schenectady or of the developmental work in Detroit. However, a listing of some of the announcements originating with the Company may be helpful to those interested in this subject. The first, which apparently is no longer available, was the most complete and consisted of a large packet of pictures and printed material (26). Subsequent releases include the announcement in *Nature* (27) and the announcement by Bridgman (28), who became a consultant for the General Electric Research Laboratory shortly after the initial announcement was published. A constant trickle of minor bits of information from General Electric followed. One of the most interesting of these appeared in the "News-scripts" section of *Chemical Engineering News* (28a). It stated:

> Starting materials apparently are not the most critical factor in General Electric's process for using high pressures to make synthetic diamonds from other forms of carbon (C. & E. N., February 21, 1955, page 718). One curious G. E. scientist, realizing that even a 49-cent jar of peanut butter contains a healthy amount of carbon, recently tried to make diamonds out of peanut butter—and succeeded.

A major news release was issued by General Electric on October 22, 1957 (29), announcing that 100,000 carats of industrial diamond grit had been produced to date, that the material was available for sale at $4.25 per carat, and that an expected $3\frac{1}{2}$ million carats were to be produced during 1958.

The General Swedish Electrical Industry (30) has announced the successful synthesis of diamonds. This company reports that its first diamonds were

produced on the 15th of February, 1953. To quote Liander, manager of their design department,

> They consisted of about 40 small crystals . . . and they were genuine beyond doubt. This was proved in several ways, among them the extremely reliable x-ray method. On the whole they were cube-like and colorless and faintly tinged with green. The experiment has since been repeated several times, again with successful results. The pressure was then calculated to be 80,000 to 90,000 atmospheres, and the maximum temperature was perhaps 5000°F.

There have been no official announcements concerning the synthesis of diamonds by well established concerns other than those of General Electric and ASEA (Allmänna Svenska Electriska Aktiebolaget, Västerås, Sweden). However, there are current rumors that success in this endeavor has been achieved by several other American and European companies.

Literature pertinent to the problem of diamond synthesis has been summarized to the year 1911 by von Fersmann & Goldschmidt (31). Additional references are given by Mellor (32). Some references of interest in this work since the year 1924 are given in references (33 to 42).

In connection with the synthesis of diamonds the question arises as to whether or not synthetic materials with properties superior to those of diamond might be made. Wentorf (43) recently reported the preparation of a cubic form of boron nitride that rivals the diamond in hardness and is more resistant to oxidation at high temperature. Details of the process have not been given, but it is assumed that the process is closely related to that being used for diamond synthesis at General Electric.

There is no doubt that an adequate supply of industrial diamond grit at reasonable price is in the offing. The transformation this may bring to American industry may almost amount to an industrial revolution!

Geology.—The importance of high-pressure, high-temperature research to geology is quite obvious. Pressures of 200,000 atm. correspond approximately to depths of 400 miles within the earth. Although the temperature existing at such depths is not known with certainty, the temperatures that can be generated at high pressures in the laboratory are certainly as large as those which exist at this depth. Laboratory synthesis of high-pressure minerals can give an accurate estimate of the depth at which such minerals are formed within the earth.

The synthesis of a material of density greater than quartz has been reported by Coes (44). Coes found several systems that would produce this material at high pressure and high temperature. The best reaction mixture found consisted of equal parts of dry sodium meta-silicate and diammonium phosphate. This material was heated at a temperature of 750°C. under a pressure of 35,000 atm. for a period of 15 hours. The yield of coesite (the name now given to the material) was about 30 mg. The density of this material is 3.01 and its refractive index 1.60 compared to a density of 2.66 and a refractive index of 1.55 for quartz. An outstanding property of this new

dense silica is that it is not attacked by long heating in hydrofluoric acid. As yet, coesite has not been found in nature. Additional work on coesite has been reported by Robertson *et al.* (45).

The synthesis of several high-pressure minerals, including all the garnets found in nature and some new ones not previously known, aluminum silicates, pyroxines, epidote minerals, and others, have also been reported by Coes (46). Wentorf (47) has discussed the formation of Gore Mountain garnet and hornblend at high temperature and pressure. Robertson *et al.* (45) have determined the stability relations of jadeite at pressures to 25,000 bars and temperatures to 1200°C. Griggs & Kennedy (10), utilizing apparatus previously referred to, have reported phase boundaries in the region bounded by 40,000 atm. and 1000°C. for the systems: gibbsite/diaspore+water, aragonite/calcite, jadeite+water/analcite, coesite/quartz, diaspore/corundum+water, pyrophyllite/sillimanite+quartz+water, pyrophyllite/kyanite+quartz+water, and kyanite/sillimanite. A review of silicate systems, as well as some new experimental work under hydrothermal conditions, has been given by Roy & Tuttle (48).

Undoubtedly high pressure phases exist at great depths within the earth that do not exist on the earth's surface. High pressure laboratory studies should elucidate the nature of these phases and eventually help to explain more clearly some of the seismic phenomena. The possibility of the existence of phases with vastly different properties than the parent material was touched off by a paper of Wigner & Huntington (49) which calculated the approximate minimum pressure that would be required to transform solid hydrogen into a metallic form. This pressure was of the order of 250,000 atm. At the time their paper was written, such pressures were outside the scope of available techniques. However, today such pressures are within the realm of possibility. Papers which have some bearing on the nature of the earth's interior are listed in references (50 to 53).

Superconductivity as a function of pressure.—Superconductivity is a phenomenon of metallic conductors in which electrons, moving through under an applied emf. at very low temperatures, instead of meeting resistance due to obstruction of their paths by the metallic atoms, move as a wave function harmonically linked to the vibrations of the atoms in such a way as to reduce the resistance to flow to an immeasurably small value (54). The ability of a metal to assume the superconducting state depends upon several factors, including what might be termed its coupling coefficient to the electron, the free volume in the crystals, the natural frequency of the atoms, and the valence, which must be odd and preferably 3, 5 or 7. Among these determinants, pressure may have an influence on three of them, i.e., the free space between the atoms, their natural frequency, and their valence.

In general, if there are polymorphic transitions induced in a metal, by pressure the higher pressure forms will have greater density and therefore less free volume than those at lower pressures, so that pressure should reduce the temperature of transition to the superconducting state and in some

cases eliminate it. When no crystal transformation occurs the compression of the lattice may not necessarily reduce the transition temperature.

It has been observed that it is more difficult for heavy atoms to assume the superconducting state than for light, probably because of the low natural frequency of the heavy atoms. Because of the asymmetry of the pressure-density curve it would be anticipated that pressure on heavy metals should increase the temperature of transition by increasing the frequency of vibration of the atoms.

The third possible influence of pressure is to force a valence electron into an unsaturated inner orbital, thus changing the valence from an unfavorable to a favorable number.

Concerning the influence of pressure on the natural frequency of the atoms, and consequently on the temperature at which a metal becomes superconducting, Mase (55) has discussed the observations of Kamerlingh Onnes that pressure decreases the temperature of transition and concludes that in these cases the lowering of the temperature is consequent upon a change in lattice vibrations in an unfavorable direction. A study by Fisk (56) shows good agreement between observation and theory for tin but poor for thallium. However, the pressures used were very small, viz., only up to 115 atm. Gaber and Mapother (57), in a more detailed study of the influence of pressure on the transition temperature for tin, found that $dT_c/dP = 4.40 \pm .20 \times 10^{-5}$ degree/atm. up to 100 atm., which indicates that the tin atom has a natural frequency on the low side of the most favorable, and consequently a rise in pressure raises T_c. Chester and Jones (16) observed that T_c for tin varies approximately linearly with pressure up to 17,500 atm. They show a negative influence of pressure on T_c for thallium. In addition, they observed that bismuth can become superconducting under high pressures.

It is known that where a metal may have an unfavorable crystal structure or unfavorable valence for superconductivity, by alloying it with another element that gives a favorable average valence or a more open crystal structure, it may become superconducting, and to date alloys have been found that become superconducting at higher temperatures than any of the pure metals. Alekseevskii and co-workers (58 to 58c), in addition to studying pure bismuth and cadmium, have given attention to alloys, especially those of gold and bismuth, bismuth and potassium, and bismuth and lithium. In the case of Au_2Bi and Bi_2K, which have monotypical lattices, T_c increases with pressure for the Bi_2K but decreases for Au_2Bi. Since this difference cannot be attributed to changes in the lattice, it is explained as due to a change in the electron concentration. If this is true, alloys deficient in bismuth should have a negative value for dT_c/dP, which was found to be true for BiLi. For Bi_3Ni they found that the transition temperature rises with pressure according to the equation $dT_c/dP = 5.4 \times 10^{-5}$ degree atm.$^{-1}$.

No case involving electronic allotropy has yet been studied. It has been proved that the large transition in bismuth is due to a change in lattice structure (59).

Electrical resistance of conducting materials under pressure.—Relatively few papers on electrical conductivity of materials under pressure or on the theoretical explanation of observed results have appeared since the extensive review of recent work in the field of high pressures by Bridgman (60) and the more recent edition of his book (6, 14). Several theoretical attempts to explain the influence of pressure on resistance were covered in the 1946 review, some of which showed qualitative agreement with segments of the experimental data, but no one of which can be regarded as entirely satisfactory. In general, electrical resistance decreases with increase in pressure, but there are striking exceptions, specifically, calcium, strontium and lithium, which give trouble to the theories.

As an extension of former measurements to higher pressures and in preparation for planned subsequent measurement to 100,000 kg./cm.^{2}, Bridgman measured the electrical resistances of 29 metals and intermetallic compounds to 30,000 kg./cm.^{2} (61). The resistances decrease with pressure for all except the intermetallic compound Ag_2Al. Most of the elements show a decreasing reduction in resistance as the pressure increases to higher values, but eleven showed virtually constant decrease with increasing pressure.

In 1952 Bridgman (13) published resistances of 72 elements, compounds, and alloys to 100,000 kg./cm.^{2}, following this in the next year by measurements on numerous elements to the same pressure but at temperatures up to 200° (62). His third paper in this series was confined to 20 compositions of bismuth and tin and 5 of bismuth and cadmium (63). This study was followed in 1954 by measurements on 13 binary alloys (64). In the same year he published resistance and compression measurements on 7 rare earth metals unavailable at the time of earlier studies. The metals in this group were samarium, dysprosium, holmium, erbium, thullium, ytterbium and lutecium. To use Bridgman's words (65), the rare earth metals show "an unusual constellation of anomalies." Numerous first-order transitions have been observed with these metals, but most of the transitions are observable only by electrical resistance measurements and these appear to be associated, at least in part, with movement of electrons from the conduction band down into lower unsaturated orbitals of higher energy. This has been most clearly demonstrated with cerium where there is a large volume and resistance break between 7 and 12,000 kg., and where it has been shown that there is no change in the crystal structure. Two other elements, viz., gadolinium and ytterbium show an irreversible change in both resistance and volume. The literature does not reveal that this increase in density has been studied by mechanical or electrical means. If the irreversibility should involve a transfer of outer electrons to inner orbitals, it would be of great scientific interest. The purposes of this review would not be served by detailing the numerous anomalies observed, but it should be mentioned that in all of the rare earths sluggish changes are characteristic and sometimes, as in the case of erbium, a first-order transition is smeared out all the way from 20,000 to 100,000 kg. There will be work for theoreticians in this field for years to come.

Kapustinskii (53) has discussed this electronic allotropy, which he has termed electronic isomerization, and particularly has applied it to geophysical problems. He divides the influence of pressure on the electronic shells into two regions. In the first, extending up to about 120,000 atm., electrons are forced from outer orbitals into unfilled higher energy positions. At much higher pressures, in accord with modern thinking, he postulates that the orbitals become completely "crushed" and the atoms lose their chemical identity. On the basis of this thinking he divides the earth into three zones: zone (a), the geosphere, extends to about 100 km. depth where the periodic laws are obeyed and the normal chemical properties are retained. In zone (b) the lower limit of which is not clearly definable, chemical properties are changed by electronic allotropy but reactions occur and compounds exist much as at the earth's surface. On the other hand, on zone (c), the centrosphere, all of the atoms have lost their chemical identity and exist only in the "universal metallic state." Kapustinskii supports his hypothesis with thermodynamic, quantum mechanical, and seismological data.

In view of Bardeen's (66) success in explaining the six hundredfold decrease in electrical resistance of single crystal tellurium with increase of pressure to 30,000 kg., where it was shown that tellurium is a typical semiconductor in which the normal energy gap between the filled band and the conduction band is 0.29 ev. and decreases with pressure to 0.015 at a pressure of 30,000 kg., Bridgman undertook a study of the effect of pressure on 7 semiconducting oxides plus germanium and silicon in both the n and p conditions (67). Measurements were made to 50,000 kg. using silver sulfate as the "hydrostatic," pressure-distributing material. The oxides studied were ZnO, Mn_3O_4, NiO, TiO_2, V_2O_5, U_3O_8, Fe_2O_3, $NiTiO_3$. No common type of behavior was observed and reproducible data were hard to obtain. Bridgman feels that all that can be hoped for is a qualitative picture which may help in establishing a working hypothesis. The electrical resistance may change in either direction by a factor of 10 or even more. Usually, however, resistance decreases at room temperature and at 200°, with the exception of Mn_3O_4. The decrease in resistance at 200° is generally smaller than that at room temperature. Theoreticians can find data here to fit almost any hypothesis!

One of the most comprehensive studies on the electrical resistance of metals to date is that by Lawson (68) who has analyzed the data extant in an effort to find scientific bases for the various types of behavior observed.

Germanium has been subjected to intensive study for a number of years due to its theoretical and industrial importance, and there are three papers within recent years devoted to the influence of pressure. Hall, Bardeen & Pearson (69) studied the electrical resistance of p-n junctions of germanium and applied Shockley's theory of the resistance of such a junction, in which the resistance is regarded as proportional to $\exp(E_g/kT)$ where E_g is the energy gap between the valency and conduction bands. The measurements over a range of 10,000 lb./sq. in. show a $\Delta R_0/R_0$ of 12.5 per cent which corresponds to a change ΔE_g of approximately 3.1×10^{-3} ev. Also, measurements made at different temperatures yield an energy gap of about 0.72 ev.

Taylor (70) measured the electrical resistance of germanium between 297–475°K. and at pressures up to 4500 lb./sq. in. Over this small range of pressure the resistance varies linearly with pressure and at 300°K. $\Delta R/R = 10.2 \pm .04 \times 10^{-5}$/atm.

Three years later Paul & Brooks (71) raised the upper pressure in similar measurements to 30,000 kg./cm.² at 25°–76°C., and also measured the influence of pressure on resistance up to 7000 kg. at −195°C. The results indicate an increase in the total energy gap up to 15,000 kg. at a rate in good agreement with earlier experiments. Above 15,000 kg. the n-type germanium shows a rapid rise in resistance regardless of purity. The explanations were based on a decrease of electron mobility with increase in pressure and a concomitant deionization of impurities. In the following year Paul & Pearson (72) made similar measurements on pure single crystal silicon and found that, in contrast to germanium, the energy gap between the conduction and the valence bands decreases with increase in pressure.

Ionic conduction of crystals has received attention from Mennonöh & Jost (73, 74), from Kurnick (75), and from Yanagimoto (76). In the first reference the object was to study the influence of the transition from a pure crystal to a mixed crystal on the pressure coefficient of the electrical conductivity. Both silver chloride and silver bromide were used as the pure crystal and increasing amounts of $PbCl_2$ were added. As was predicted, the pressure coefficient decreases as the amount of lead chloride is increased. Mennonöh & Jost (74) made similar studies at 250° to 300° and up to 10,000 atm. but using solid solutions of silver chloride and lead chloride on the one hand, and silver bromide and lead bromide on the other. For the silver chloride solid solutions, the conductivity decreases with increase in lead chloride toward a limiting value, while with the silver bromide-lead bromide solid solutions, the conductivity increases to a maximum and then decreases as lead bromide is added.

Kurnick studied the concentration of defects in the silver bromide lattice by treating it with cadmium bromide to block the vacancies. The temperature was maintained at 300° and the influence of pressure was studied up to 8000 kg./cm.² By observing the mobilities of the Ag ions and of the vacancies, it was concluded that the molal volume, ΔV, of imperfections at this temperature amounts to 16 cc./mole. The free volumes associated with these motions were found to be reduced by 2.7 and 7.4 cc./mole, respectively. The ΔV is uninfluenced by the Frenkel disorder type.

The ionic conductivity of $K_4Fe(CN)_6$ was measured by Yanagimoto who found that as the pressure is increased a minimum of conductivity occurs at 1410 kg./cm.²

Karpov (77) prepared 99.4–99.8 per cent pure diamagnetic AgO and measured electrical resistance at pressures up to 12,000 kg./cm.² at 20°. At the maximum pressure and 20° the specific resistance was found to be 7×10^{-2} ± 15 per cent. It was concluded from the fact that the temperature coefficient between −40° and +20° is positive that this compound is an electronic semiconductor.

Magnetic effects of pressure.—In his 1946 review, Bridgman (60) cited nine papers on the interaction of pressure and magnetic properties of ferromagnetic materials. In general the effect of applying pressure at constant field is to decrease the flux, often by very large amounts. A 30 per cent nickel alloy was reported to be rendered nearly nonmagnetic by pressure of 12,000 kg./cm.² Evidence was cited that the Curie temperature for ferromagnetic materials is independent of pressure while other data lead to the conclusion that this point can be displaced by measurable amounts.

Bader (78) in 1953 published a discussion of the influence of pressure on the Curie point for iron and nickel as interpreted from Heisenberg's Exchange Integral. In the following year Sawaguchi (79) published a study of the two-dimensional influence of pressure on the Curie point with barium titanate, in which he observed that the Curie point may be expressed as a function of pressure according to the equation $T_c = 120 + 3.1 \times 10^{-5} P^2$. His interpretation of the results was that the influence of one- and three-dimensional pressure on T_c can be accounted for satisfactorily by the Clausius-Clapeyron equation, but for the two-dimensional application of pressure this equation is inadequate. He concludes that there might have been some secondary effects in Forsberg's experimental results other than pure two-dimensional pressure (80).

In the same year Patrick (81) made a very extensive study of pressure and the Curie point, using iron, cobalt, nickel, gadolinium, a 96:4 ferrosilicon, 90:10 ferrosilicon, the alloys compensator, invar, permalloy, monel, alumel, and a manganese-zinc ($Mn_{.5}Zn_{.5}Fe_2O_3$) and a lanthanum-strontium ferrite ($La_{.75}Sr_{.25}MnO_3$). In these materials the Curie point ranged between 16° for gadolinium and 1120° for cobalt. The results disagree with two common forms of interaction curves, and those for iron do not agree with Kornetzki's predictions based on measurements of volumetric magnetostriction. In the same issue of *The Physical Review*, Smoluchowski (82) reviews the experiments of Patrick and finds a fair agreement between them and theory based on a Brillouin function.

The affect of pressure on ferroelectric phenomena in sintered barium and strontium titanates was studied by Michels & van Meurs (83). In this case the dielectric constant of sintered $(Ba,Sr)TiO_3$ was determined at 1000 cycles and between 25° and 150° at pressures up to 3000 atm. In each case studied the dielectric constant, when measured as a function of temperature, rises rapidly to a maximum and then falls off hyperbolically as if following a Curie-Weiss law, $\epsilon = c/(T - T_p)$. The influence of pressure was found to be a broadening of the maximum, a reduction of its height and a displacement toward lower temperatures. For example, when the pressure was atmospheric the maximum was found to be at 57° while at a pressure of 3000 atm. the maximum was attained at 45°. Empirical qualitative conclusions on the height and the position of the maximum are drawn.

The saturation magnetization of nickel as a function of pressure was studied by Jones & Stacey (84), who used pressures up to 10,000 atm. and

fields to 12,000 oersteds. In addition they tested the hypothesis that some nonferromagnetic materials under sufficient pressure might become ferromagnetic. No evidence for such a transformation was found with palladium, platinum, molybdenum, tungsten, copper, silver, or gold. In no case did the volumetric susceptibility exceed 0.0006 at low-field intensities or 0.0003 at the highest field intensities.

An interesting paper by Benedek & Purcell (85) reports on the nuclear magnetic resonance observed in liquids by the "spin-echo" or free-precession technique using pressures up to 10,000 atm. and studying solutions in water, pentane, hexane, toluene, ethyl iodide, and methyl iodide as the solvents. In all of the solvents the proton relaxation time was found to decrease with increasing pressure, a behavior which was explained by the assumption that the dominant relaxation mechanism involves a coupling between the nuclei and the intramolecular fields and therefore the relaxation time is at least partially determined by the rotational freedom of the molecule, which obviously would be reduced by increasing pressures. A study on the influence of pressure on the Curie point of barium titanate single crystals (86) led Merz to the conclusion that the lowering of the Curie point by pressure gives the same results as shrinking the lattice would through the substitution of strontium for barium. Up to 25,000 atm. $dT_c/dP = -5.8 \times 10^{-3}$ degree/atm.

The first-order transition point near 0°C. decreases with pressure up to 1500 atm. and subsequently rises again.

Miscellaneous electrical phenomena.—Some miscellaneous electrical phenomena associated with pressure have been studied during recent years. For example, Michels & Perez (87) observed the displacement of the Piezoelectric frequency of quartz by pressure. Two quartz plates were used of 942 and 6040 kilohertz. For these the rate of change of frequency with pressure was 8.03×10^{-6} cm.²/kg. and -2.03×10^{-6} cm.²/kg., respectively. It was suggested that oscillating quartz plates might be used for the determination of pressure inside closed vessels. Wall & Gill (88) investigated the influence of pressure on transference numbers for electrolytes and found that 1000 bars produce a slight increase in the transference number for hydrogen ion in N/10 HCl but approximately a 2 per cent decrease for K ion in N/10 KCl and a still larger decrease for NaCl.

Considerable interest has been shown in the effect of pressure on the dielectric constant. For earlier literature the reader is referred to Bridgman's 1946 review. Recently Reitzel (89) has determined the effect of pressure on the dielectric constant of vitreous silica between 25° and 138° and at pressures to 4000 kg./cm.² The molecular polarization was found to decrease linearly with pressure with a slope that is independent of temperature. The relative decrease in polarization was found to be -1.6×10^{-6} kg./cm.²

Alekseevskii & Brandt (58b) have studied the effect of pressure on the Hall effect. With bismuth of purity 99.9996 per cent, no influence of pressure on the Hall effect was observed, but with bismuth containing 0.02 per cent lead, a maximum in the curve of Hall effect vs. temperature was found be-

tween 30° and 40°K. They speculated that this maximum is due to a dependence of the concentration of conducting electrons on the pressure.

It was observed by Braun (90) that a pressure of oxygen has no effect on phosphors, at least up to 150 kg./cm.^{2} However, large mechanical pressure does change the behavior of phosphors, an influence that has been ascribed by Braun to rupture of the phosphor crystals.

Pressure induced by shock waves or by a detonating explosive.—In general, pressures that can be attained in the advancing front of a shock wave in a gas do not run higher than the source and therefore shock waves are not a promising source of pressures for scientific study. On the other hand, temperatures in shock waves may exceed 10^4 °K. and when combined with the pressure make a unique region for study even though phenomena are exceedingly transient. More rewarding for the study of simultaneous high temperature and high pressure is the detonation of explosives where indications are that pressures of the order of several hundred thousand atmospheres concomitant with temperatures of several thousand degrees may be attained. Here, also, the time interval is extremely short and yet some molecular processes are so rapid as to go virtually to completion in the time available. Only detonations of solid or liquid explosives provide pressures in the high range.

In 1952 Hikita (91) published a useful review of detonation covering theory of mechanisms, equations of state, internal energy, and compositions of the products.

The measurement or calculation of Chapman-Jouguet pressures in detonation of numerous experimenters, a selected list of which is:

Sakurai (92) who described a method of measuring the velocity of the wave front in trinitrotoluene and found a pressure of approximately 60,000 kg./cm.^{2}, in good agreement with theory. Duff & Houston (93), who measured the pressure and reaction zone in a detonating explosive; Nahmani & Manheimer (94), who observed a velocity of 6000 meters per second, a temperature of 4000°K., and a pressure of 89,000 atm. in detonating nitromethane; Hikita & Kihara (95), who have calculated pressures and other properties of detonating explosives by use of an equation of state of their own devising. Temperatures and pressures for trinitrotoluene, tetryl, pentrite-NaCl, pentrite-NH_4NO_3, TNT-NH_4NO_3, $Hg(ONC)_2$ and $Hg(ONC)_2$-$KClO_3Pb(N_3)_2$.

In 1956 Noddack & Grosch (96) reviewed methods of measuring explosives and temperatures and gave seven tables of data. By the relatively recent method of maximum surface pressure using one-gram compressed charges they found surface pressures between 11,400 and 14,300 kg./cm.^{2} for four metallic triazides and mercuric fulminate. Cook & Keyes (97) measured the pressures in detonating granulated trinitrotoluene by means of the acceleration of a metal slug. Peak pressures observed ran to about 4500 atm. The last of this series is an important paper on detonation pressure measurement by Schall (98) who concludes that an upper limit to the Chapman-Jouguet pressure can be assigned for any explosive. He avers that the real pressures

during detonation come to within 20 to 30 per cent of this upper limit, which for nitropenta is 310,000 atm. and for hexolite 300,000 atm. Newer measurements by the method of free surface yield approximately 40 per cent higher pressure; therefore the maximum pressure in the detonating wave front goes up to 400,000 atm. The actual peak pressure is reported as approximately two times the Chapman-Jouguet pressure. On the other hand, Schall concludes that the peak pressure in solids has little significance. He reports that an Abel-type equation of state serves qualitatively very well.

Other than one industrial process making use of a detonated explosive for compacting powdered metals prior to sintering, no recent use of explosives for the study of high pressure effects has been made except in studies of explosives themselves. Nevertheless, the substantial progress in the understanding of phenomena in a detonating explosive within the past decade has made a real contribution to the science of high pressures, especially through attention given to the equation of state. It would seem that electronic allotropy might well be studied in a detonating explosive through its probable effect on the velocity of detonation and through density changes observable by means of high-speed x-rays. Accepting Schall's conclusion that a detonating wave front may go to 400,000 atm., such a technique would make available a new region of pressure at, as yet, unattained temperatures.

Equation of state.—Customarily, the starting point for the determination of an equation of state serviceable in connection with the detonation velocity of an explosive, at least for a solid explosive, has been one of the three equations derived by Fürth (99), by Pack, Evans & James (100), or by Murnaghan (101). Fürth's equation is complicated and difficult to use but satisfactorily fits extant data for solids at very high pressures.

Pack, Evans, & James' equation was suggested by quantum mechanical considerations and is relatively simple, involving only two assignable constants. Murnaghan's equation, derived from elasticity theory for solids, is the simplest of all with but one arbitrary constant, though the sum of the two measurable elastic constants may be used as an arbitrary value for fitting data.

For equations of state for gases under extreme pressure, reference should be made to Kihara & Hikita (102), and a later paper by Hikita (103), who have applied their equation of state to the calculation of the velocity of shock waves in air, iron and lead. A critical review of the classical theory of detonation waves is presented, giving theories for detonation in finite charges, the time dependence of detonation, detonation failures, etc.

In 1954 F. Cramer (104) published an empirical equation for extremely high pressure and applied it to several gases. He gave derivations of the thermodynamic quantities: potential, free energy, internal energy, enthalpy, entropy, and the two specific heats. The equation contains only three arbitrary constants and is said to be in error at 3000 atm. by less than 1 per cent. In the same year Murgai (105) derived an equation for the detonation velocity as a function of loading density.

As pointed out by Cook (106), who also derived an equation of state for extreme pressures from hydrodynamic theory of detonation, nearly any reasonable equation can be satisfactory for condensed explosives due to the inaccuracy in the measurements of detonation velocities.

An entropic equation of state applicable to shock waves was published by Duvall & Zwolinski (107) in 1955.

Perhaps the most important work going on at present in an effort to establish the pressure-volume-temperature relations in a gas is that of Saurel & Vodar (108), who are attempting high precision measurements to 10,000 atm. and 1000°C.

The influence of pressure on radioactive decay.—It is probable that pressures of any magnitude so far attained in the laboratory will have little or no influence upon radioactive decay involving only intranuclear reactions. On the other hand, a large number of artificially radioactive isotopes are known in which decay may occur through the capture of an orbital electron and the subsequent emission of a neutrino. In such cases of radioactive decay any external influence that affects the electronic configuration of the orbitals surrounding the nucleus or the number of electrons in these orbitals should have an influence upon the rate of radioactive decay. This radioactive decay, called K capture, because the K electrons are closest to the nucleus and are therefore the most frequently captured, should be proportional to the density of electrons near the nucleus, which in turn should be influenced by pressure.

The chemical transformation of an atom to an ion should make sufficient difference in the electronic density, especially for light atoms, to be observable in rate of radioactive decay. The lightest element showing K capture is beryllium, and in 1949 Segré & Wiegand (109) demonstrated that BeO decays more slowly than metallic beryllium. Bauchez *et al.* (110) demonstrated that beryllium fluoride decays more slowly than beryllium. Subsequently, Bainbridge (111) made a very careful comparison between the rates of radioactive decay of beryllium metal, beryllium oxide and beryllium fluoride, and found that the metal decays 0.13 per cent faster than the oxide and 0.74 per cent faster than the fluoride. This means that the oxide will decay 0.61 per cent faster than the fluoride, which is consistent with what we know about the separation of charge in these two compounds. In addition they found that T_c^{99m} decays more rapidly as potassium tecnetate than as tecnetium sulfide. The pure metal electroplated onto nickel and reduced in hydrogen also decays more rapidly than the sulfide.

To date no paper has been published giving experimental data on the influence of pressure on K capture. However, a private communication from Bainbridge (112) states that he has been working on this problem. Mr. Barney Gogarty, at the University of Utah (113) has found a demonstrable effect of pressure on the decay of beryllium 7 in beryllium chloride and at present is working on the influence of pressure on K capture by gallium.

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OPTICAL ROTATORY POWER[1]

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EXISTENCE OF TWO GROUPS OF PROPERTIES OF OPTICALLY ACTIVE SUBSTANCES

There are two groups of properties of optically active substances which are of great interest to different branches of science. The first group which is the main subject of this paper is the optical rotatory power, closely related to circular dichroism.

The second group of phenomena is based on the difference of diastereomeric substances, i.e., of compounds which are formed if the *d*-antipode of one optically active substance is combined with the *d*- or the *l*-enantiomorph of a second optically active substance. These differences, e.g., the differences in solubility *et al.* of diastereomeric substances, are fundamental for the preparation of pure optically active substances and to the occurrence of these substances and their associated metabolism in living organisms in which optical activity is of vital importance.

It would be of significant interest if these two groups of properties could in a general way be correlated with each other. The limited relationship and the reasons for this status have recently been reviewed (1). The problem is only mentioned here, with the added remark that the particular behaviour of very weak absorption bands, discussed in the following, would play a great part in such considerations.

RELATIONS BETWEEN ROTATORY POWER, CIRCULAR DICHROISM, ORDINARY OPTICAL ABSORPTION AND THE ANISOTROPY FACTOR

It is useful, before discussing the special case of weak absorption bands, to call to mind some definitions, and to mention some relations which hold for optical rotatory power and circular dichroism in general.

First it should be noted that optical rotatory power is physically equivalent to circular birefringence, i.e., to the property of having a different index of refraction n_r for right hand and n_l for left hand circularly polarized light. The rotation ρ produced by a layer 1 cm. in length is related to the circular birefringence $n_l - n_r$ by the relation

$$\rho = \frac{\pi}{c} \nu(n_l - n_r) \qquad \qquad 1.$$

c being the velocity of light *in vacuo* and ν the frequency of the light employed.

The index of refraction for ordinary light and correspondingly for circularly polarized light of frequency ν is connected in a quantitative way with the existence, intensity, and frequency of the absorption bands of the substance for ordinary and for circularly polarized light. Rotatory power, i.e.,

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circular birefringence, is for this reason quantitatively related to the exist-ence, intensity, and frequency distribution of the difference of the absorp-tion power for right and left hand circularly polarized light. If the molecular rotation $[M]_\nu$ is expressed in degrees, we have the general relation (2, 3)

$$[M]_\nu^0 = 2.1 \times 10^3 \frac{n_\nu^2 + 2}{3} \nu^2 \int_{\nu_1=0}^{\infty} \frac{1}{\nu_1} \frac{3}{n_{\nu 1}^2 + 2} (k_l - k_r) \frac{d\nu_1}{\nu_1^2 - \nu^2} \qquad 2.$$

In this equation, n_ν and n_{ν_1} represent the index of refraction for light of frequency ν, viz., ν_1 of the medium which may be a gas, a pure liquid, or a solu-tion of the optically active substance. If M is the molecular weight of the substance, the molecular rotation $[M]_\nu$ is related to the specific rotation $[\alpha]_\nu$ by the relation

$$[M]_\nu = [\alpha]_\nu \cdot \frac{M}{100} \qquad 3.$$

while the specific rotation $[\alpha]_\nu$ is by definition connected to the observed rotation α (in degrees), the length d of the (liquid or gaseous) layer in deci-meters and p the number of grams of active material present per 100 ml. by the equation

$$[\alpha]_\nu = \alpha \frac{100}{d \cdot p} \qquad 4.$$

k_l and k_r in equation 2 are the molecular absorption coefficients of the op-tically active substance for left and right hand circularly polarized light of frequency ν_1. The exact definition of the molecular absorption coefficient k_r is given by the statement that the intensity of a beam of right hand cir-cularly polarized light of frequency ν_1 will on passing through x cm of a solu-tion of concentration C gm mol/liter, decrease from J_0 to

$$J = J_0 \, 10^{-k_r C \cdot x} \qquad 5.$$

The integral in equation 2 has to be taken over all values of ν_1. Equation 2 thus states that the molecular rotatory power $[M]_\nu$ of a given substance for any frequency can be found by integration as soon as the circular dichroism $(k_l - k_r)$ as a function of the frequency has been empirically or theoretically determined.

It is thus an important feature of optical rotatory power that it is the sum of contributions made by the various parts of the dichroism spectrum which occurs in the same frequency regions where ordinary optical absorp-tion is observed. For the latter reason, it can even be stated that every re-gion of ordinary absorption makes its contribution to rotatory power.

It is of interest to compare $(k_l - k_r)$ which is according to equation 2 decisive for the rotatory contribution with the mean value

$$k = \frac{k_l + k_r}{2} \qquad 6.$$

k is, specifically, the absorption coefficient of the racemic substance for ordi-nary light. Place

$$\frac{k_l - k_r}{k} = g \qquad 7.$$

g is according to this definition approximately equal to the relative difference of the absorption coefficients for left and right hand circularly polarized light; it depends, in general, on the frequency ν. It has been called the anisotropy factor (4). [Dissymmetry factor would have been a better designation.] Its physical meaning will be discussed carefully in a later section. The product $k \cdot g$ may be introduced instead of $(k_l - k_r)$ in equation 2 for the calculation of the rotatory power.

HOMOGENEOUS ABSORPTION BANDS

A simplification of the general relation (equation 2) results in many cases from the circumstance that g is often in the region of isolated absorption bands, practically constant, or, more accurately, equal to

$$g = g_0 \frac{\nu}{\nu_0} \qquad\qquad 8.$$

where ν_0 is the frequency corresponding to the center of the absorption band. A region of absorption which shows this simple behaviour will in the following be called a homogeneous absorption band. An example is represented in Figure 1. It shows the ordinary absorption k, the circular dichroism $k_l - k_r$ and the anisotropy factor g in the region of an ultraviolet absorption band, due (in first approximation) to the N_3-group of dextrorotatory azidopropionic dimethylamide in hexane (5). In the region of the absorption band near 2800 A $k_l - k_r$ follows closely the course of k, but $k_l - k_r$ is very small in the region of more intense absorption which lies on the short wavelength side of the band.

In the case of an isolated homogeneous absorption band, it is natural and possible to consider the rotatory contribution of the absorption band, i.e., the value of $[M]_\nu$, obtained from equation 2 if the integral at the right hand side of this equation is restricted to the frequency region of the isolated absorption band. The result is shown in Figures 2a and 2b. In Figure 2a the case $k_l > k_r$ is considered. The rotatory contribution is in this case positive at the long wavelength side of the band; it passes through a maximum inside the absorption band at the long wavelength side of the center, passes through zero in the middle of the band, reaches a negative extreme and consequently decreases to zero in the region of very short wavelengths. The entire phenomenon of circular dichroism and corresponding rotatory contribution is called Cotton effect (6); the Cotton effect is called positive if $k_l > k_r$ (case of Figure 2a), and negative if $k_l < k_r$ (case of Figure 2b). A given antipode of an optically active substance always has absorption regions with a positive and other absorption regions with a negative Cotton effect, in such a way that the integral of $(k_l - k_r)d\nu/\nu$, taken over the entire spectrum, vanishes (summation rule).

As far as the ordinary absorption in the region of an isolated absorption band is concerned, the intensity is usually and in a comprehensible way measured by the f-value of the absorption band. The f-value, or number of dispersion electrons, responsible for the absorption band is related to the in-
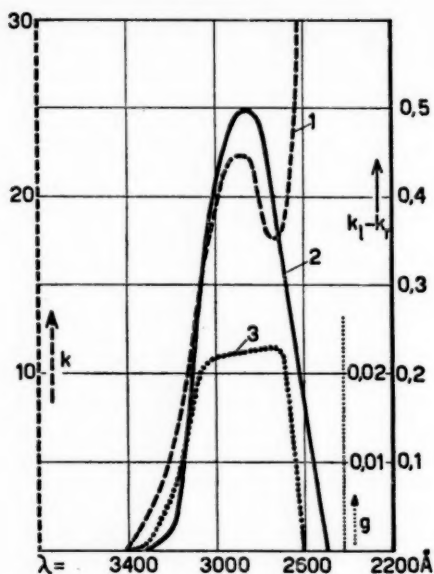
FIG. 1. Azidopropionic-dimethylamide [CH₃CHN₃CON(CH₃)₂] in hexane. Curve 1: Ordinary absorption (k); Curve 2: Circular dichroism $(k_l - k_r)$; Curve 3: The anisotropy factor $g = (k_l - k_r)/k$.
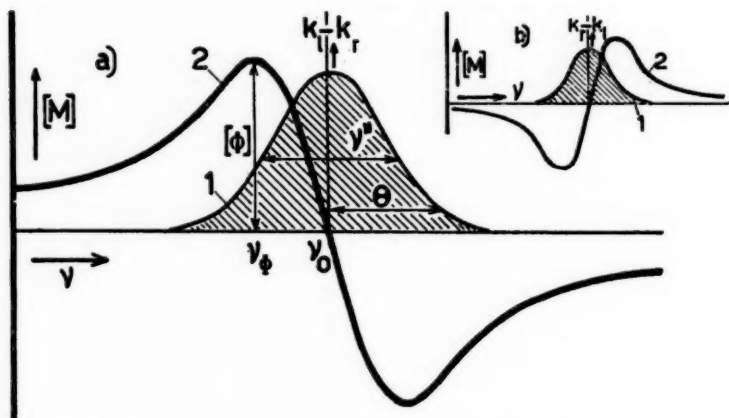
FIG. 2a and 2b. Rotatory contribution and circular dichroism of isolated absorption band with Gaussian shape. 2a) Positive Cotton effect $[k_l > k_r]$. 2b) (Reduced scale) Negative Cotton effect $[k_l < k_r]$.

tegral of the molecular absorption coefficient, taken over the absorption band in question by the equation

$$f = 1.44 \cdot 10^{-19} \int_{\text{absorption band}} \left(\frac{3}{n_0^2 + 2}\right)^2 n_0 k d\nu \qquad 9.$$

It is known that the order of magnitude of the f-values is, for the most intense organic dyes, equal to one. For the N_3-absorption band of α-azido-propionic dimethylamide near $\lambda = 2900$ A, represented in Figure 1, f equals 4.7×10^{-4}. It is also known that the sum of the f-values corresponding to the entire optical spectrum is equal to the number of valency electrons contained in the atoms which build up the molecule. It follows that the N_3-absorption band in Figure 1 represents only a vanishingly small portion of the total optical absorptive power of the molecule or even of the N_3-group.

Homogeneous isolated absorption bands with Gaussian intensity distribution.—The evaluation of the integrals representing the rotatory contribution and the f-value of a homogeneous isolated absorption band can be reduced to the application of simple standard expressions in the normal case where the frequency dependence of k or of $k_l - k_r$ can be approximated by a Gaussian curve, i.e., by an expression of the form 3(7)

$$k = k_{\max} \cdot e^{-((\nu_0 - \nu)/\theta)^2} \qquad 10.$$

ν_0 and $k_{\max}$ being the frequency and the value of the molecular absorption coefficient corresponding to the center and θ a parameter responsible for the width of the absorption band. (See Figure 2a.) θ is related to the half width ν'' of the absorption band, i.e. to the distance between the points to the right and left of the absorption maximum at which $k = \frac{1}{2}k_{\max}$ by the relation

$$\nu'' = 2\sqrt{\ln 2}\,\theta = 1.665\,\theta \qquad 11.$$

The f-value of an absorption band of the shape indicated by equation 10 is then

$$f = \left(\frac{3}{n^2 + 2}\right)^2 n \cdot 2.54 \cdot 10^{-19} k_{\max} \cdot \theta = \left(\frac{3}{n^2 + 2}\right)^2 n \cdot 1.52 \cdot 10^{-19} k_{\max} \cdot \nu'' \qquad 12.$$

If the band is really homogeneous, i.e., if the anisotropy factor in the region of the absorption band is represented by equation 8, the contribution of the band to the molecular rotatory power $[M]$ in degrees is equal to equation 3

$$[M]^0_{\text{contribution}} = 3723 \cdot g_0 k_{\max} \frac{\nu}{\nu_0}\left[e^{-((\nu_0-\nu)/\theta)^2} \cdot \int_0^{(\nu_0-\nu)/\theta} e^{x^2}dx - \frac{\theta}{2(\nu_0+\nu)}\right] \qquad 13.$$

The values of the function $e^{-x^2}\int_0^x e^{x^2}dx$ occurring on the right hand side of equation 13 are tabulated (8). The maximum contribution of the absorption band designated in Figures 2a and 2b by $[\phi]$ occurs, according to equation 13 for

$$\nu = \nu_\phi = \nu_0 + 0.9\theta \quad \text{and} \quad \nu_0 - 0.9\theta \qquad 14.$$

$[\phi]^0$, i.e., the value of $[M]^0$ for $\nu = \nu_\phi$ is (in circular degrees) approximately equal to

$$[\phi]^0 = 2014 \cdot g_0 k_{\max} \qquad 15.$$

Equation 13 shows that the rotatory contribution of an absorption band, whose center has the frequency ν_0, is known as soon as the anisotropy factor g_0, the value of $k_{\max}$ and the width parameter θ are known. Equation 15 shows that the maximum rotatory contribution $[\phi]$ at $\nu = \nu_\phi$ is in a simple way determined by the same parameters and that especially g_0 can be easily found if $[\phi]^\circ$ and $k_{\max}$ have been determined.

If the absorption spectrum of a substance contains, in addition to the isolated absorption band (whose center has the frequency ν_0), a number of further absorption bands, the rotatory power actually observed will, according to equation 2, be the sum of a number of positive and negative contributions, each contribution having approximately the shape of Figure 2a or 2b.

As an example the rotatory dispersion observed in the case of a solution of α-azidopropionic-dimethylamide in ether equation 3 is represented as curve 1 in Figure 3. The ordinary optical absorption is shown in curve 2. It is, for the purpose of further analysis, approximated by curve 2', corresponding to equation 10; with $k_{\max} = 22.4$; $\nu_0 = 1.03.10^{15} (\lambda_0 = 2900$ A); $\theta = 0.866.10^{14}$ sec^{-1} ($\nu'' = 1.44.10^{14}$ sec^{-1}, $\lambda'' = 430$ A). If we put $[\phi] = 1100^\circ$, we obtain from 15: $g_0 = 0.024$. The rotatory contribution of the N_3-absorption band near $\lambda = 2900$ A, calculated on the basis of equation 13, is then given by curve 3. The difference between curve 1 and curve 3 is curve 4. It represents the contribution of the absorption bands in the distant ultraviolet below 2600 A. Curve 4 has the shape of a "normal" rotatory dispersion curve. We note the agreement of the value of $g_0 = 0.024$ calculated from $[\phi]^0$ and $k_{\max}$ on the basis of equation 15 with the value of g_0, determined according to Figure 1 by direct measurement of the circular dichroism in hexane solution. This agreement and the absence of any anomaly in curve 4 of Figure 3 prove the correctness of the analysis.

A more detailed example, showing the decomposition of the observed rotatory power into a sum of contributions made by the various absorption bands, is given in Figures 7a to 7d. From these examples it is evident that the anomaly produced in the rotatory dispersion curve by an isolated homogeneous absorption band is so characteristic that it is usually possible to carry out graphically, with reasonable accuracy, the decomposition of the observed rotatory dispersion into a contribution corresponding to Figure 2a or b and into a contribution which is free from a rotatory anomaly in the region of the absorption band. The graphical resolution practically consists in the determination of the maximum rotatory contribution $[\phi]^\circ$ of the band at a frequency ν_ϕ; see equations 14 and 15. The combination of $[\phi]^\circ$ with $k_{\max}$ gives, then, immediately the anisotropy factor g_0 of the absorption band. The circular dichroism $k_l - k_r$ can then, with the aid of equations 7, 8, 10 be indicated for the region of the isolated absorption band in question. This means that it is possible, from measurements of the optical rotation and of the ordinary light absorption, to predict quantitatively the value of the circular dichroism.

This way of determining the anisotropy factor or the circular dichroism
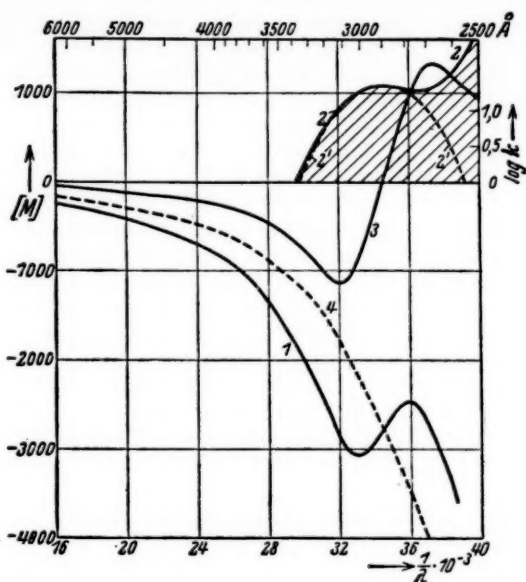
FIG. 3. Azidopropionic-dimethylamide [$CH_3CHN_3CON(CH_2)_2$] in ether. Curve 1: Molecular rotatory power [M] observed. Curve 2: Molecular absorption coefficient observed. Curve 2': Absorption band (with Gaussian error curve shape), which is used as basis for computing curve 3. Curve 3: Rotatory contribution of the absorption band (curve 2 or 2') due to the azido-group. Curve 4: Difference of curve 1 and 3; significance: rotatory contribution from the remaining absorption bands of the molecule.

in the region of an isolated absorption band is not as exact, nor as reliable, as the direct measurement of the circular dichroism (9) which is no more difficult than the measurement of rotatory dispersion. It will be seen in the following paragraphs that not all absorption bands are homogeneous in the sense of equations 7, 8. A vigorous scrutiny of the data reveals that no homogeneous absorption band has yet been observed. Equation 10 and the equations 13 and 15 are approximations also. Deviations from the Gaussian form of the absorption curve 10 are easy to detect; they are usually small and the validity of equation 15 is not much affected by them. However, the fact that the anisotropy factor is in many instances, even where k is well represented by equation 10 not constant, can make the application of equation 2 instead of equation 13 necessary. A fair homogeneity of an isolated absorption band may be assumed in those cases where the rotatory contribution of the absorption band, determined graphically, is zero at the center of the absorption band and has its maximum values [ϕ] at the frequencies

ν_ϕ indicated by equation 14. Deviations in the location of these frequencies prove the nonhomogeneity of an absorption band. Even by this control, only a practical homogeneity can be ascertained; strong deviations of g, provided they are limited, e.g., to border regions of extremely small absolute intensity, will not be detected by measurements of the rotatory dispersion; measurements of the circular dichroism alone are in this respect reliable.

THE PHYSICAL SIGNIFICANCE OF THE ANISOTROPY FACTOR

A positive or negative Cotton effect of a particular absorption band arises if the vibrating moment corresponding to an optical absorption band has nonparallel noncoplanar components in distant parts of the molecule. All physical theories of optical rotatory power agree with respect to this general statement.

It has, in continuation of original work by Born (10) and by Oseen (11) been shown by Kuhn (12) that the simplest vibrating moment able to produce a Cotton effect consists of two components which are a distance d apart and directed at right angles to each other and to the distance d. This simplest mode of vibration is shown in the left hand part of Figures 4a and 4b respectively.

Besides the vibrating system, in which the arrows located in point 1 and 2, symbolize the change of momentum in unit time occurring in point 1 and 2, the spatial distribution of the electric vector δ of a right hand circular wave is represented in Figures 4a and 4b. A system possessing a vibrating moment, according to Figure 4a, and oriented with the direction of d parallel to the direction of propagation of the beam of circularly polarized light, is seen to give a more intense interaction than the system in Figure 4b. In the case where $d = \lambda/4$ (λ = wavelength of the incident light) and where the absolute magnitudes of the components of the vibrating moment in point 1 and 2,
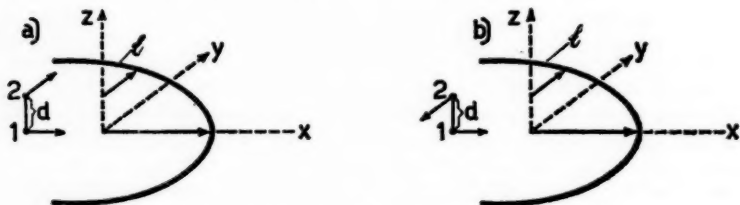
FIG. 4a and 4b. Effect of right circularly polarized light (represented at the right hand part of Figures 4a and 4b) on a system whose vibration mode consists of two components at right angles to each other located at points 1 and 2, respectively (arrows at points 1 and 2). The distance d between 1 and 2 is here put equal to $\lambda/4$. 4a) The mechanical energy transferred to the partial momentum in point 1 adds to the energy transferred to the partial momentum in point 2. The vibrating system responds strongly to right circular light. 4b) The mechanical energy transferred to the partial momentum in point 2 is of opposite sign to the energy transferred to the partial momentum in point 1. The vibrating system does not respond to right circularly polarized light.

in Figures 4a and 4b, are equal, it is observable that the amount of energy transferred to the system by the lightbeam in points 1 and 2, respectively, will add up in the case of Figure 4a and cancel in the case of Figure 4b.

A change of the orientation of the models (Figures 4a and 4b) with respect to the direction of the incident light by 180° does not alter the difference in their response to right (or left) hand circularly polarized light and a difference is correspondingly left, even if the models are oriented at random with respect to the the direction of propagation of the light.

The qualitative result also remains if the distance d of points 1 and 2 in Figures 4a and 4b is assumed to be different from $\lambda/4$. In actual molecules d will be much smaller than $\lambda/4$. In this case the circular dichroism $k_l - k_r$ will still be a maximum if the partial momenta in points 1 and 2 of Figures 4a and 4b are at right angles to d, and to each other, and of equal magnitude, the anisotropy factor g being optimum for these assumptions and, for random orientation of the model, equal to

$$g = \frac{2\pi d}{\lambda} \qquad 16.$$

For the optimum orientation, as represented in Figures 5 and 6 the anisotropy factor would be twice the value 16.

The situation remains qualitatively the same if the vibrating moment of a given absorption band consists of more than two components, or if the values of the partial momenta present are unequal and at other angles than those assumed in Figures 4a and 4b. In all these cases, including the actual case in which the partial momenta are continuously distributed over the molecule, the anisotropy factor of a given absorption band is a unique function of the spatial and angular distribution of the corresponding vibrating momentum. If the spatial and angular distribution of the vibrating momentum remains the same, the anisotropy factor will remain identical, and vice versa. The statement according to which the anisotropy factor remains constant in the region of a homogeneous absorption band, is, therefore, identical with the statement that the spatial and angular distribution of the vibrating momentum is the same in all parts of the absorption band. Optical activity is a means of obtaining information with respect to this distribution.

High Value of the Anisotropy Factor in the Case of Extremely Weak Absorption Bands

The anisotropy factor has been determined in a number of absorption bands of both inorganic and organic substances, either directly by measuring $k_l - k_r$ and k separately (equation 7), or by combining the rotatory contribution $[\phi]$ with the maximum intensity k_{max} of the absorption band (equation 15). Some results of such determinations are compiled in Table I.

It is seen from this table that anisotropy factors as high as 0.1 are sometimes observed; it is, however, seen that high values are exclusively observed in the case of absorption bands with extremely small f-values.

A tentative application of equation 16 to potassium chromotartrate

(the last example in Table I) gives for an absorption band of this substance near $\lambda = 5800$ A $d = 80$ A. This is a value for d which exceeds the actual molecular diameter at least by a factor 20. At one time the possibility was suggested (13) that the vibrating electrical momentum of very weak absorption bands might be localized at the extreme outside regions of the molecule, where the electronic density is small. This possibility was tested

TABLE I

Observed Values of Anisotropy Factors g and f-Values of Absorption Bands

Substance	Solvent	λ(A)	f-value	g	Reference
[Co(en)$_3$]Br$_3$	water	4657	$1.08 \cdot 10^{-3}$	0.031	(25)
[Co(ox)$_3$]K$_3$	water	5700	$9.2 \cdot 10^{-4}$	0.043	(26)
CH$_3$—C—(CH$_2$)$_5$CH$_3$ with H above and ONO below	water	2500	0.5	$<10^{-5}$	
	Hexane	3650	$9 \cdot 10^{-4}$	0.01	(27)
	Hexane	2300	0.1	$<10^{-5}$	
CH$_3$CHN$_3$CON(CH$_3$)$_2$	Ether	2800	$4.7 \cdot 10^{-4}$	0.024	(5)
CH$_3$CHN$_3$COOCH$_3$	Alcohol	2900	$3.9 \cdot 10^{-4}$	0.0065	(3)
Camphor	Hexane	2900	$8 \cdot 10^{-4}$	0.10	(22)
Aldehydo-d-glucose-penta-acetate	Chloroform	2930	$5.8 \cdot 10^{-4}$	0.034	*
Pulegone	Cyclohexane	3240	$1.5 \cdot 10^{-3}$	0.044	†
		2450	0.23	$<10^{-4}$	
Postassium chromo-tartrate	water	5800	$3 \cdot 10^{-4}$	0.09	(13)

* Hudson, H., Wolfrom, M. L., and Lowry, T. M., *J. Chem. Soc.* **136,** 1179 (1933)

† Lowry, T. M., Simpson, D. M., and Allsopp, C. B., *Proc. Roy. Soc.* (*London*) [A] **163,** 483 (1937)

by observing the influence of a high velocity gradient on the rotatory power of the solution.[2] No measurable effect was observed with velocity gradients as high as 10^3 sec^{-1}; the conclusion derived from this result was that no regions outside the usual molecular domain could be responsible for the appearance of high values of the anisotropy factor of very weak absorption bands.

The real physical reason for the experimental rule, evident from Table I,

[2] Unpublished measurements, carried out in 1932.

was later discovered in an attempt to calculate the rotatory power and the absolute configuration of an inorganic substance (14).

Applying the results to an absorption band whose vibrating moment consists of two components, it can be stated that the systems represented in Figures 4a and 4b correspond to an optimum with respect to the value of $k_l - k_r$, not however, to an optimum with respect to $(k_l - k_r)/k$. It is found that a strong increase of the anisotropy factor is obtained if the two components localized in points 1 and 2 of Figures 4a and 4b continue to be of the same magnitude, to lie in a plane perpendicular to d, and are chosen to be
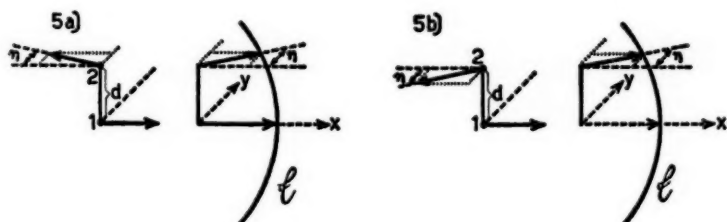
FIG. 5a and 5b. Effect of right circularly polarized light (represented on the right hand side of Figures 5a and 5b) on a system whose vibrational mode consists of two components, nearly antiparallel to each other, located at points 1 and 2, respectively. The distance d between 1 and 2 is small compared with λ. 5a) The mechanical energy transferred to the partial momentum in point 1 is not entirely cancelled by the energy transferred to the partial momentum in point 2. The vibrating system responds to right circularly polarized light. 5b) The mechanical energy transferred to the partial momentum in point 1 cancels exactly with the energy transferred to the partial momentum in point 2. The vibrating system does not respond to right circularly polarized light.

nearly antiparallel (instead of at right angles) to each other. The orientation of the two momenta, thus obtained, is indicated in Figures 5a and 5b. The component of the vibrating moment localized in point 1 is here, again, assumed to be oriented at a given time in the positive x-direction, while the component localized in point 2 is vibrating in a plane, parallel to the x-y-plane at a small angle η with the negative x-direction.

If a right hand circular wave is assumed to propagate in the direction of d (z-axis of Figure 5), as in the case of Figure 4, and if

$$\eta = 2\pi d/\lambda \ll 1 \qquad\qquad 17.$$

it is seen that the energy transferred to the vibrating system is in the case of Figure 5b exactly equal to zero, and small, but definitely different from zero in the case of Figure 5a. This means that the system Figure 5b, in the orientation chosen for this figure, does not respond to a right hand circular wave, while a small, but finite, response exists for Figure 5b and a left hand circular wave (or for Figure 5a and a right hand circular wave). We, therefore, have a total circular dichroism, i.e.,

$$k_l \neq 0; \qquad k_r = 0 \qquad\qquad 18.$$

(orientation corresponding to Figure 5b)

or

$$g = \frac{k_l - k_r}{\frac{1}{2}(k_l + k_r)} = 2 \qquad\qquad 19.$$

(orientation corresponding to Figure 5b)

If a random orientation of the vibrating system, with respect to the beam of light, is assumed instead of the optimum orientation of Figure 5, there will be no total dichroism. An optimum value of the anisotropy factor

$$g = \sqrt{2.5} = 1.58 \qquad\qquad 20.$$

is in this case obtained if

$$\eta = \eta_m = \frac{2\pi}{\sqrt{2.5}} \, d/\lambda \simeq 4d/\lambda \qquad\qquad 21.$$

(optimum condition for random orientation and $d \ll \lambda$)

We note that in the case of complete orientation (equation 18), even if the linear dimensions of the vibrating system are arbitrarily small compared with the wavelength of light, a total circular dichroism can be obtained and that for random orientation (equation 20) values of g as high as 1.58 can be realized. This value again is independent of the ratio d/λ. This ratio is, according to equation 21, only of importance in choosing the value of η to produce the g-value of equation 20.

The g-value 1.58 (equation 20) corresponds, according to the definitions of equations 7 and 6 to $k_l/k_r = 8.5$, a very remarkable dichroism.

Generalizing the explanation of g-values given in the special cases of Figures 4 and 5, the sign and value of the anisotropy factor is entirely determined by the repartition and orientation of the components of the vibrating moment in the molecule; it is independent of the mechanism which is supposed to produce this repartition.

Two effects can be considered to be responsible for these mechanisms. One of them corresponds to the theory of coupled oscillators (8, 10, 11, 12, 15) which takes into account the action of the electric field of a vibrating moment, localized in a first approximation in one part of the molecule, e.g. in point 1 of Figure 4a on the rest of the molecule, e.g., on a polarizable group localized in point 2 of Figure 4a. The second one is the one electron theory (16 to 20) which encompasses the fact that the vibrating moment according to wave mechanics is, even in first approximation, distributed over the entire region in which the ψ-function corresponding to the electron in question, is different from zero.

It can be shown (21) that the contribution of coupling to optical activity will dominate in most cases. The one electron contribution formally corresponds to higher approximation terms of the coupling effect. Only in special cases, presumably with very weak absorption bands, there may be exceptions where the one electron contribution will reach a magnitude comparable to the value of the coupling effect.

A correlation between the occurrence of high values of the anisotropy

factor and the intensity (f-value) of the corresponding absorption bands, does not appear explicitly from equations 20 and 21. The existence of a connection is in reality qualitatively seen from equation 21.

For $d = 10^{-8}$cm, $\lambda = 6 \cdot 10^{-5}$cm, e.g., we obtain from 21:

$$\eta_m = 4 \; \frac{\cdot 10^{-8}}{6 \cdot 10^{-5}} = 0.67 \cdot 10^{-3} \text{ (radians) or } 2' \, 18'' \qquad 21a.$$

A small value of η (and equal magnitude of the partial momenta localized in points 1 and 2 of Figure 5) means that the vibrating moment of the absorption band in question is very nearly a quadruple-moment. The f-value of a vibration like Figure 5 will thus be very small compared with the f-value which would be observed, if the partial vibration localized in point 1 were alone instead of being in phase with another component localized in point 2 of Figure 5.

If $f_1 = f_2$ are the intensities (f-values) which would be observed if the charges vibrating in points 1 and 2 of Figure 5 were vibrating independent of each other, the f-value of the coupled vibration represented in Figure 5 would, again for random orientation of the model, be

$$f = f_1 \eta_m^2 / 2 \qquad 21b.$$

or for $f_1 = 1$ and $\eta_m = 0.67 \cdot 10^{-3}$:

$$f = 2.2 \cdot 10^{-7} \qquad 21c.$$
$$\text{(for } \eta = \eta_m \text{ and } f_1 = 1)$$

In order to reach $g = 1.58$ (equation 20), i.e., the maximum value possible for random orientation, we would thus require an f-value as low as 10^{-7}. The f-values (Table I) of the weakest absorption bands actually investigated are of the order of magnitude $f = 10^{-4}$, or 1000 times higher than 21c.

We may assume that f_1 and f_2 (the intensities which would be observed if the charges in points 1 and 2 of Figure 5 were vibrating independent of each other) will again be equal and approximately equal to 1 in these weak absorption bands, but that η in Figure 5 will exceed the value indicated in equation 21. We will in this case have

$$g = \frac{4\pi d}{\sqrt{3}\lambda} \; \frac{1}{\sqrt{f}} \Big] \qquad 22.$$

$$f \cdot g = \frac{4\pi d}{\sqrt{3}\lambda} \; \sqrt{f} \Big] \qquad 22a.$$

[valid if $f_1 = f_2 = 1$ ($|m_1| = |m_2|$ in Figure 5); random orientation of the model Figure 5 towards the beam of light; f-values higher than 10^{-6}, or more generally $\eta > > 2\pi d / \lambda$].

It is seen from equation 22 that if the condition $f_1 = f_2 = 1$ is fulfilled, the anisotropy factor will be proportional to $1/\sqrt{f}$; it will be great if f is small, which is in agreement with the experimental rule of Table I.

Computation of d for potassium chromotartrate with the use of equation 22 and the data from Table I gives $d = 1.25$ A, instead of 80 A with the use of equation 16. The values of g actually observed are thus elucidated by the consideration inherent in equation 22.

The consequence of the occurrence of high values for g in the case of weak absorption bands is that the rotatory contribution of weak bands in the visible is as important as the contribution of strong bands, especially where weak absorption bands are situated in the near, and strong bands in the far, ultraviolet. The importance is enhanced by an extensive mutual cancellation of the far ultraviolet contributions.

The predominant role of weak absorption bands brings us to an understanding of the frequently encountered high sensitivity of optical rotatory power to chemical or physical changes. It is indeed evident from Figure 5 that a physical or chemical change need only add a slight component, e.g., in the y-direction, to the vibrating moment existing in point 2 or 1 of the system, in order to produce a great relative change in the value, or even a change of the sign, of the small angle η which is decisive for the anisotropy factor and thereby for the rotatory contribution of the band. A change in η of the same magnitude in the case of Figure 4 would leave the rotatory contribution of the band practically unaltered. Weak absorption bands must be extremely sensitive as far as their rotatory contribution is concerned while strong absorption bands are in this respect less alterable.

Nonhomogeneous Absorption Bands

In some cases the anisotropy factor varies markedly, or even changes its sign, in the region of an isolated, apparently simple, absorption band. As an example the data for camphor (22) are represented in Figure 6. It is seen that the anisotropy factor is small in the short-wave region of the absorption band situated near 2900 A and high in the long wave part of it.

This change of the anisotropy factor indicates that the angular and spatial distribution of the vibrating moment is not the same in the different parts of the absorption band. The electronic change associated with the absorption process must therefore be of a different character. The conclusion is obvious that the absorption band near $\lambda = 2900$ A is in reality the superposition of at least two absorption bands, both being due in first approximation to the C—O group. The result is confirmed by the experimental observation of a weak absorption band clearly discernible at the long wave end of the 2800 A absorption band in acetaldehyde (23) and by the existence of a corresponding weak independent system in the absorption spectrum of formaldehyde vapour (24).

Other examples of nonhomogeneous absorption bands are the long wave bands of inorganic complex salts of the type $[Co(en)_3]$ $Br_3(25)$ and $[Co(ox)_3]$ K_3 (26) where en = ethylenediamine and ox = oxalic acid, and the absorption band near 5800 A in an alkaline solution of chromium tartrate (13).

An unsolved problem.—A further example which illustrates the disclosure of the nonhomogeneity of an absorption band through the anisotropy factor and which at the same time offers an unsolved problem is β-octyl-nitrite. $CH_3CH(ONO)C_6H_{13}$.

The ordinary absorption (curve 1 in Figures 7a and 7b) (27) shows an apparently uncomplicated absorption band near 3600 A, characteristic of the ONO-group, with some fine structure, the main band consisting of five
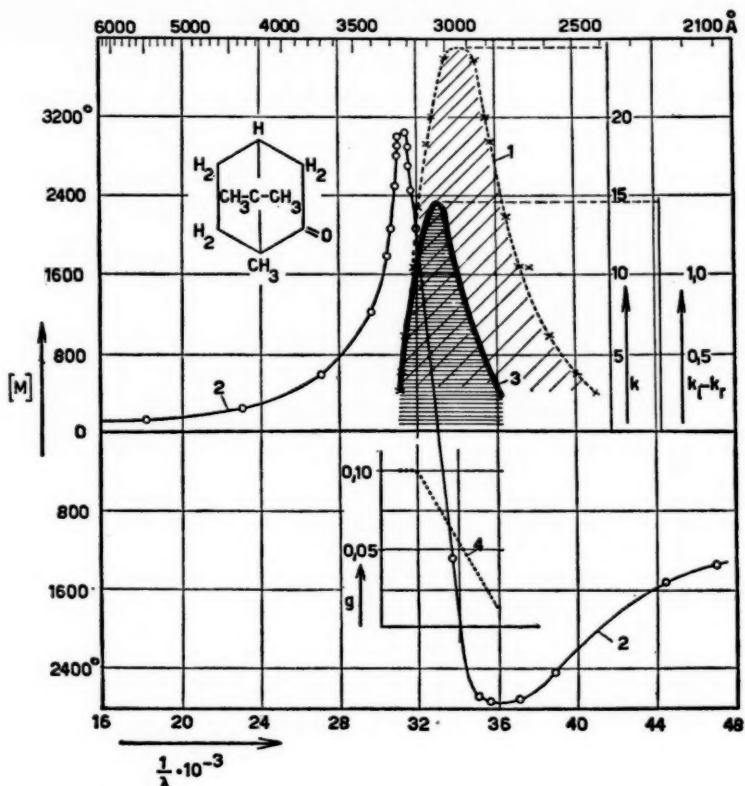
FIG. 6. d-Camphor in hexane. Curve 1: The observed absorption. Curve 2: The observed rotation. Curve 3: The observed circular dichroism. Curve 4: The anisotropy factor.

narrow bands. Comparison with the circular dichroism (curve 2 in Figure 7b) discloses, in addition to this fine structure, a nonhomogeneity. There exists, in the long wave part of the band, a broad region of low intensity (curve 6 in Figure 7c) with positive dichroism, free from any fine structure while each of the five narrow bands mentioned has a negative Cotton effect. The absence of fine structure in one band and its presence in another part of the absorption region proves, in addition to the difference in the sign of the anisotropy factor, that the two parts of the absorption region must be due to a thoroughly different electronic transition. The absence of fine structure in one part of the absorption region may indicate that the absorption of the corresponding light quantum is followed by an immediate decomposition of the molecule, while the presence of fine structure in the other part indicates a longer lifetime of the excited state. The investigation of the optically
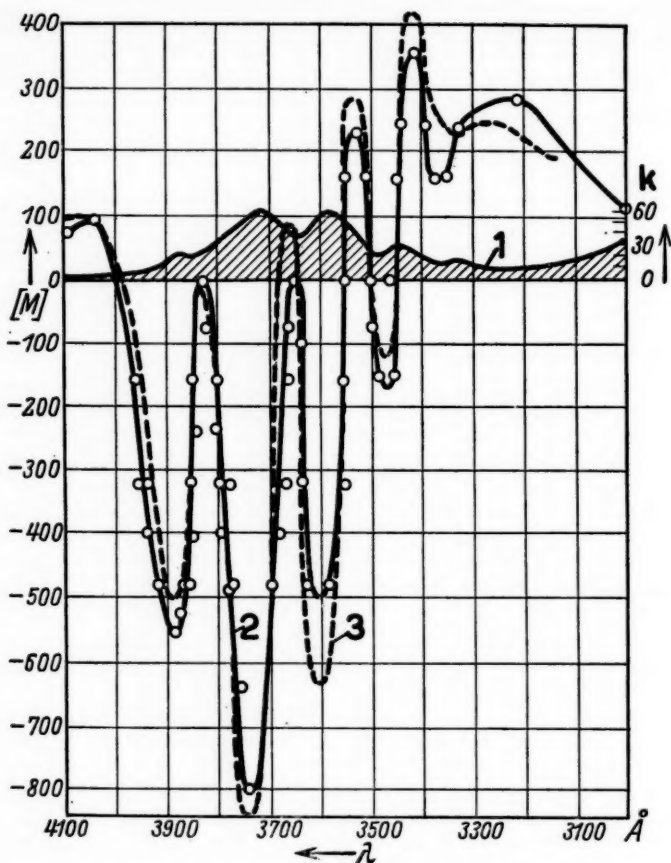
Fig. 7a. β-Octylnitrite in hexane. Curve 1: The observed absorption. Curve 2: Molecular rotation. Curve 3: The rotation calculated [the sum of the contributions curves one to six represented in Figure 7d].

active behaviour may thus become a source of information which might otherwise be difficult to obtain. A full discussion would, of course, involve the repartition of the electric moment as well as the lifetime and other properties of the excited state corresponding to the various parts of the absorption region.

The main problem connected with Figures 7a to 7d is the behaviour of the anisotropy factor in the region of the five narrow absorption bands mentioned. It is seen from Figure 7b that circular dichroism reaches a maximum at the frequencies corresponding to the maximum of ordinary ab-

sorption of each of the narrow bands. Furthermore, it is seen that the aniso-
tropy factor near the middle of each of the narrow bands is practically the
same (if correction is made for curve 6 in Figure 7c). This means that the
repartition of the vibrating moment corresponding to the center of each
of the narrow bands is practically the same. Physically this observation
obviously means that the electronic transition is common to all the narrow
bands. The difference in frequency of the bands is due to internal vibration
superimposed on the electronic transition. The identity of the anisotropy
factor in the center of the various narrow bands then corresponds to the
statement that the vibrating moment is mainly determined by the electronic
transition and only to a small extent influenced by the internal vibration of
the molecule. A similar statement holds for any isolated broad absorption
band in the region in which the anisotropy factor is constant. The more rea-
sonable this statement appears, the more it is astonishing that, according
to Figure 7b, the anisotropy factor definitely decreases if we go from the
center to the edge of each of the narrow bands. It drops, astonishingly, ex-
actly to zero midway between two adjacent bands. This decrease to zero is
also observed in methyl-cyclohexylnitrite and in methyl-phenylnitrite (28).
In the latter case, it is remarkable that the presence of five narrow bands is
not visible in ordinary absorption but is as sharp and distinct in circular
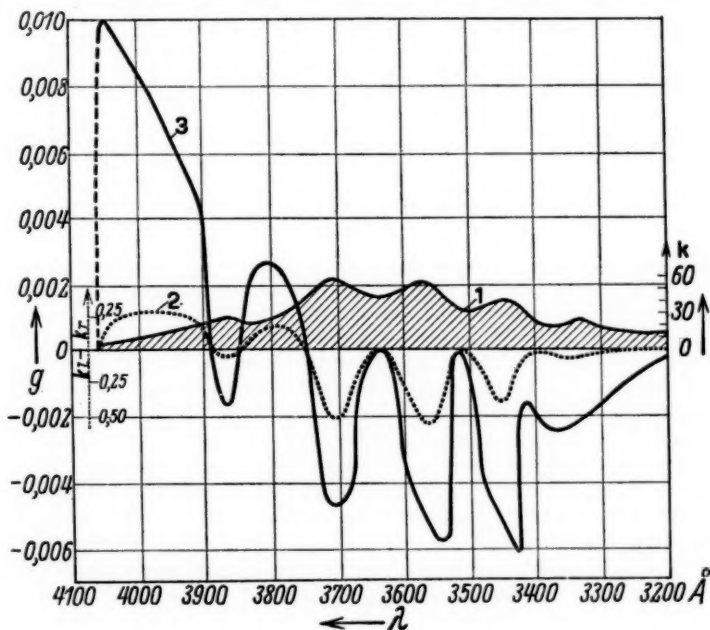
FIG. 7b. Curve 1: The observed absorption. Curve 2 (dotted): Circular
dichroism. Curve 3: Anisotropy factor.

dichroism in methyl-phenylnitrite as it is, according to Figure 7b, in the case of methyl-n-hexylnitrite. The decrease to exactly zero of the anisotropy factor between the narrow bands is in the case of methyl-n-hexylnitrite not only observed in hexane solution (Figure 7b) but also in the vapour state (29). An influence of the solvent on the repartition of the vibrating moment can, therefore, not be the true reason for the drop of the anisotropy factor. On the other hand a substantial change of the repartition of the vibrating moment must take place by going from the center to the edge of each small
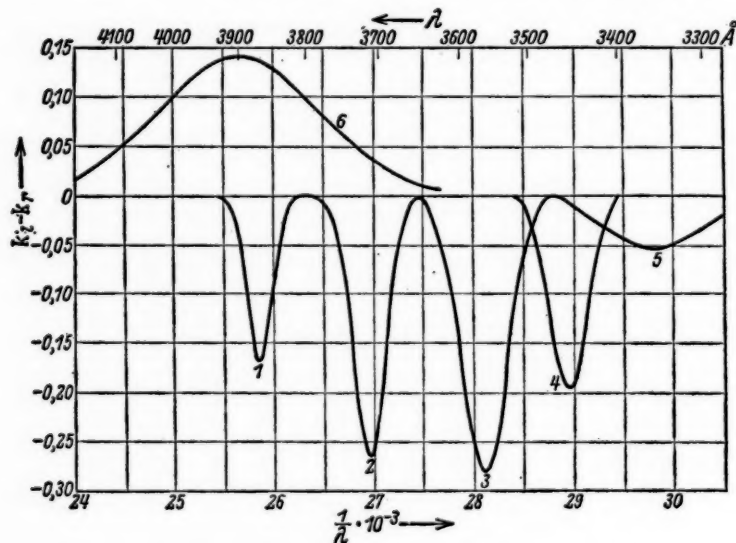
FIG. 7c. The observed circular dichroism of β-Octylnitrite (curve 2 of Figure 7b) is represented as the sum of six narrow dichroism bands numbered one to six, each of which has a Gaussian intensity distribution.

band. It can be mentioned that a decrease of the anisotropy factor to zero has also been observed in many other instances; for example, in the case of α-azidopropionic dimethylamide and in methyl-α-azidopropionate [(3) and Figure 1].

If going from the center to the edge of the small absorption bands in Figure 7b means that a mechanical rotational movement is superimposed on the electronic transition and on the internal vibration of the molecule, a certain mechanical deformation of the frame of the molecule might be conceivable. The mechanical deformation may be imagined to produce a change in the repartition of the vibrating moment of the electronic transition; it is, however, extremely improbable that the change in the reparitition of the vibrating moment should in all cases (small bands in β-octylnitrite, absorption band in azidopropionic ester and dimethylamide) be such that the
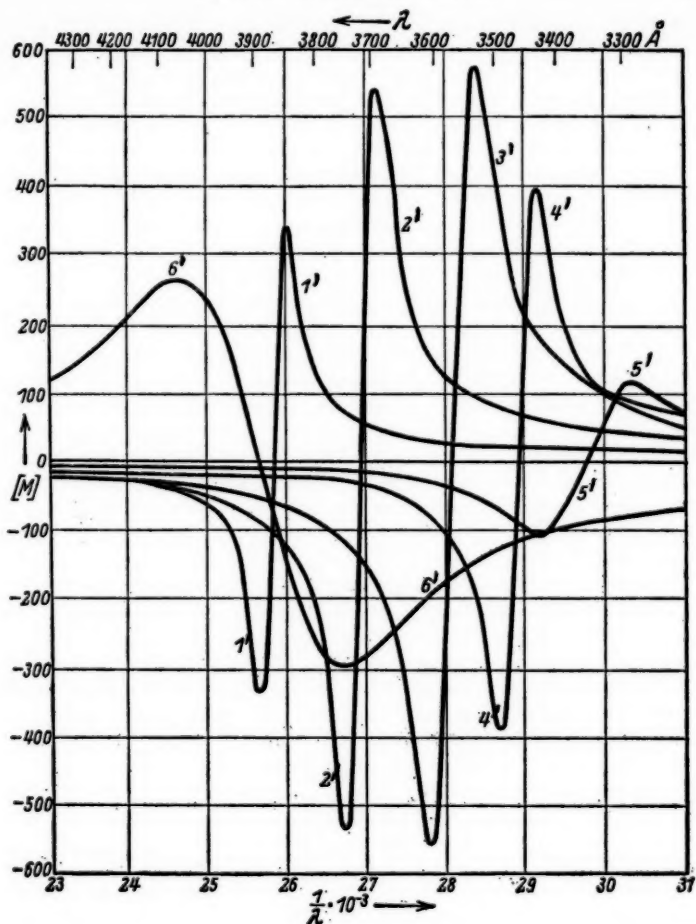
FIG. 7d. The rotatory contribution of each band, numbered one to six of Figure 7c calculated with the help of equation 13 is represented by six curves, numbered one to six, respectively. The sum of these rotatory contributions is shown in curve 3 of Figure 7a.

anisotropy factor is reduced to zero. The drop to zero must therefore be considered as an important but hitherto not understood phenomenon.

APPLICATIONS

In any investigation in which optical rotatory power is the aim, or in which it is a tool of research, the information to be obtained or to be used

is concerned with the repartition of the vibrating moment of certain absorption bands. For experimental comparison this information will be expressed by the anisotropy factor of one or more absorption bands of the substance considered.

Absolute configuration.—In the case of absolute configuration for example the problem is solved if it is possible by consideration of an appropriate model to determine the sign of the anisotropy factor of one absorption band of a given form of the model.

The antipode of the actual substance which possesses in the absorption band in question the same anisotropy factor, will have the configuration demonstrated in the model.

The recommended choice for model calculations of this type are substances possessing medium or strong absorption bands, the anisotropy factor of weak absorption bands being very sensitive to small errors in the spatial and angular distribution of the components of the vibrating moment and therefore eventually sensitive to small alterations of the model representing the actual molecule. It is important for the reliability of the consideration that the anisotropy factor of the specific absorption band be insensitive to small physical and chemical changes in both the model and actual molecule.

A calculation of the absolute configuration of methyl-ethyl-carbinol and other substances like

$$[Co(ox)_3]K_3 \quad \text{and} \quad \overset{\text{NH}_2 \quad \text{NH}_2}{\underset{\text{CH}_3 \quad \text{CH}_3}{\bigcirc \quad \bigcirc}}$$
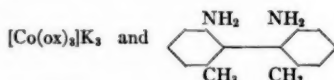
was carried out some years ago in this way (32). The result of such calculations, which in the case of methyl-ethyl-alcohol, has been confirmed by x-ray analysis (30), was reviewed a few years ago (21). According to those results it is established that D-lactic acid has the configuration

$$\begin{array}{c} \text{COOH} \\ | \\ \text{H--C--OH} \\ | \\ \text{CH}_3 \end{array}$$
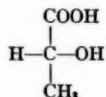
where H and OH are above, COOH and CH_3 behind the plane of the paper.

The case of 2,2'-diamino, 6,6'-dimethyldiphenyl is an example where sensitivity of the sign of optical rotation to small chemical changes has been observed (31) and where care in the model treatment is necessary (33).

Relative configuration.—In the case of relative configuration a great part of the experimental and theoretical results has been summarized by a number of rules concerning the shift of optical rotatory power produced in a given molecule by chemical substitution (15, 34). In order to predict or understand the shift produced by a chemical change, the absorption bands which are nearest to the visible and which give the highest rotatory contribution in the visible, have to be considered especially; the chromophoric groups which in first approximation are responsible for the appearance of

these absorption bands, the spatial distance of these groups from the center of asymmetry and from the place where the chemical substitution is made, will all be of decisive importance.

Representation of experimental data.—As all further discussion and evaluation has to be based on the Cotton effect or on anisotropy factors, it would be highly desirable to present any data on optical activity as far as possible in the form of statements about the intensity, width, and anisotropy factor of absorption bands (or the intensity and width of circular dichroism bands). In the case of Figure 7a, for example, the statement that there is an absorption region with a positive anisotropy and five narrow absorption bands with a negative anisotropy factor is a simpler description of the facts than an enumeration of the maxima and minima or even a full reproduction of the rotatory dispersion curve. A comparison of the optically active behaviour of methyl-n-hexylnitrite with methyl-cyclohexylnitrite and methyl-phenylnitrite is simplest in terms of the circular dichroic behaviour of the ONO-absorption band common for these compounds. Alternative descriptions are very difficult.

It has recently been proposed (35) to characterize the rotatory behaviour by an enumeration of the maxima, minima, and inflections of the rotatory dispersion in cases where a full reproduction of the curves of rotatory dispersion is not possible. The consideration of the rotatory dispersion certainly represents progress compared with consideration of the rotatory power for a selected wavelength. Since any further use which can be made of rotatory dispersion is a statement concerning the Cotton effect or anisotropy factor of the absorption bands of the molecule, it would be preferable to give the data in terms of intensities and widths of dichroic bands or else of intensities, widths, and anisotropy factors of the absorption bands measured.

As the details concerning anisotropy factors and circular dichroism are only difficultly obtained by analysis of rotatory dispersion and ordinary optical absorption, it would, in addition, be preferable to measure circular dichroism (and ordinary optical absorption) directly. It has been mentioned that slight inhomogeneities which can be of great importance will by this method be detected with far higher certainty and accuracy than by measurement of the rotatory dispersion which can in fact be calculated accurately from dichroism.

As our knowledge of absolute and relative configuration is getting more complete, the investigation of optically active data becomes a tool for elucidating the vibrating electric moment of absorption bands of chromophoric groups and for studying the orientation, the polarizabilities and the internal interaction between the groups making up simple or complicated optically active molecules (33).

Many special branches of science contributed to the elucidation of the nature of optical rotatory power; consequently, the results obtained are, and will in turn be, of interest and importance for the same branches of science, including experimental and theoretical physics, chemistry, biochemistry, and biology.

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COLLOID AND SURFACE CHEMISTRY[1,2]

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The growth and diversity of the broad field of colloid chemistry made it
necessary to exclude high polymers, rheology of disperse systems, emphasis
on many special topics such as aerosols, chromatography and ion exchange
membranes, and most of the applied literature. Instead, a path is taken
through Preparation and Stability, Interfaces at the various phase boun-
daries, Optical Properties, Surfactants, and Biological Colloids. Much
important new information has been covered in meetings and in books, a
summary of which precedes the review.

Meetings and books.—That the interest in, and development of, the vari-
ous aspects of colloid chemistry has increased at a tremendous pace is evi-
denced by the many symposia held on an international scale. In the United
States, there were the three annual National Colloid Symposia (1) and the
American Chemical Society's Symposium on Interfacial Films (2). A number
of contributions at the International Congress on Catalysis (3) also had a
direct bearing on colloid chemistry. Pertinent meetings in England sponsored
by the Faraday Society (4) were held on Flocculation and Coagulation,
Physical Chemistry of the Enzymes, and Membrane Phenomena. In addi-
tion, in England, there were the symposia on Chemisorption (5), on Vapour
Phase Chromatography (6), the Second International Congress of Surface
Activity (7), and the 3rd International Congress on High-Speed Photography
(8), the proceedings of which include only new techniques and applications
not otherwise available in published literature. German meetings of im-
portance include the Second Aerosol Congress (9), the Conferences on Sus-
pended Matter (10), the Meetings on Dust Technology (11), and on Rhe-
ology (12). Polymers, biocolloids, and polyelectrolytes in solution were taken
up at the Symposium on Macromolecules in Israel (13), while a meeting on
rheology, concerned with theories of elasticity and plasticity, was conducted
in Moscow (14).

The August-October, 1956, issue of the *Journal of Colloid Science* was
devoted to papers from the former students of Sir Eric Rideal to honor a
lifetime of service in the advancement of colloid science. Perusal of this

issue, and the papers from the symposia, "Flocculation and Coagulation" and the "Second International Congress of Surface Activity," would serve as a good survey of recent progress in, and the present status of, colloid chemistry.

Among new books, Manegold's first volume of *Allgemeine und Angewandte Kolloidkunde* (15), which has particularly good diagrams, in addition to excellent organization, promises to fulfill the need for a survey textbook. Much of the three volume set edited by Eirich on *Rheology Theory and Applications* (16) is devoted to colloidal systems. The annotated bibliography, *Light Scattering by Colloidal Solutions*, by Fishman (17) and *Tables of Light Scattering Functions for Spherical Particles* by Pangonis, Heller & Jacobson (18) have found wide use as reference books on optical properties; various optical techniques were also covered by Heavens (19) and by Oster & Pollister (20). Information on the colloidal properties of siliceous matter was collected into single volumes by Hauser (21) and by Iler (22). Solubilization phenomena were brought together by McBain & Hutchinson (23), as well as in a chapter in *Emulsion Polymerization* by Bovey and associates (24). Becher's *Principles of Emulsion Technology* (25) and Niven's *Industrial Detergency* (26) provide good explanations in terms of practical industrial problems, while biological aspects of surface phenomena were emphasized by Schulman's chapter in *Progress in Biophysics and Biophysical Chemistry* (27). Also of direct interest are *Foam Stability* by de Vries (28) and the volume devoted to colloidal precipitates of macromolecules by Audubert (29) and to boundary phenomena by Wolf (30). Although topics in surface chemistry and adsorption have been reviewed elsewhere in this series, special mention can be made here of Trapnell's treatise on *Chemisorption* (31), Hulburt's chapters in *Catalysis*, Volume II (32), Jacobs & Tompkins' chapter in *Chemistry of the Solid State* (33), the chapters by Gomer, by Becker, by Morrison, and by Suhrmann in *Advances in Catalysis*, Volume VII (34), and the comprehensive survey by de Boer in Volume VIII (35) . The book on *Molecular Structure and Biological Specificity* edited by Pauling & Itano (36) contains much material pertinent to biological colloidal chemistry.

PRODUCTION AND STABILITY

The irreversible, hydrophobic type of colloid will be emphasized most in this section. For such sols, the dispersed state exists because of energy barriers set up by the double layers or by the solvation layers, or both. The electrical repulsive forces (except for high-charge densities) had been put on a relatively sound theoretical basis in the 1940's, although it now can be stated (4) that their first formal definition belongs to Derjaguin and Derjaguin & Landau, while Verwey & Overbeek arrived at similar results only slightly later and quite independently. The repulsive action due to adsorbed layers still eludes quantitative treatment.

It has also been firmly established that the attractive forces tending to promote coagulation are of the dispersion, or London-van der Waal's, type

but their exact nature and magnitude appeared to be undecided until recently. Overbeek & Sparnaay (37), who used a sensitive cantilever balance, reported values 500 times smaller than Derjaguin & Abrikosova (38), who used a microbalance based on an ingenious electrical arrangement. This serious discrepancy led to recent independent measurements by Kitchener & Prosser (39) using a cantilever balance also, but a somewhat more sensitive one, and paying particular attention to the elimination of electrostatic changes. The results of Derjaguin & Abrikosova were confirmed. Forces of about 10^{-3} dyne/cm.^{2} for plates (forces between colloidal particles would be too small for direct determination) at a distance of 1μ are in accord with either the 1948 Casimir & Polder reduction in the London forces due to electromagnetic retardation or the generalized macroscopic treatment of Lifschitz (40). Accordingly, at distances greater than about 0.2μ, the force per unit area between plates varies *in vacuo* as the inverse fourth power, and at distances less than about 0.02μ as the inverse third power. Surface roughness and other experimental difficulties make it extremely difficult to confirm these force-distance laws exactly, particularly at the close distances. Yet the implications of these contributions to quantitative colloid chemistry are tremendous.

What might be called second-order corrections to the earlier developments of the double layer repulsive forces have multiplied. Space will permit reference to a few special treatments only, although adsorption and the electric double layer will be discussed under *Solid-liquid interfaces*. The free energy of interaction of two identically charged sols was computed electronically by Hoskin & Levine (41) and Hoskin (42) from Derjaguin & Landau's equation which treats two spherical particles as sections of two infinite parallel plates. Good approximations have been realized for large particle separations at both small and large surface potentials. The treatment at large surface potentials was particularly needed. On the other hand, Glazman & Dykman (43) concluded from calculations based on Derjaguin & Landau's approach that mixtures of uni-univalent and bi-valent electrolyte solutions should be stronger coagulants than the sum of the components; observations do not agree, indicating the need for introducing some other factor. In a test of Overbeek's treatment of the suspension effect using clay suspensions, Bloksma (44) obtained significantly smaller effects than calculated. Factors determining the point of no charge on silver halides were evaluated by Freyberger & De Bruyn (45), and by Overbeek, Watillon & Serratosa (46) who found that the sols in acetone-water mixtures obeyed the Mackor hypothesis. Derjaguin (47) developed equations relating double layer repulsion to liquid film thickness between two solids and to the "wedge effect." The water-retaining ability of clay and kaolin in terms of the effect of different sorbed ions on the "wedge pressure" was measured by Kukolev & Syrkin (48). Gupta (49) made the suggestion that on coagulation the two double layers from two particles become one triple layer.

In a carefully performed continuing series of investigations on nascent

negative AgBr and AgCl sols, Težak, Matijević & Schulz (50) developed a very simple interpretation of the Schulze-Hardy rule showing its dependence on the ionic size (the larger the ion the more influential it is) and the valency of the coagulating ions. Mirnik *et al.* (51) determined the negativity activity limit of stability of AgCl and AgBr systems at low concentrations of sodium and barium nitrates; the activity limit shifts to higher pAg values with increasing concentration of electrolyte. The progress Težak is making is all the more interesting because he avoids the theoretical approach of most investigators and because crystal formation and growth are combined with the coagulation process in his studies.

Several important contributions were made to our understanding of specific lyophobic sols from the same generalized point of view. On a copper ferrocyanide sol and later on others, Bhattacharya, Kumar & Bhattacharya (52) successfully tested their previously derived relation, $m/(c-a) = nt+1$, between the electrolyte concentration c and the time of coagulation, t, where a is the concentration to cause coagulation in infinite time, m is the excess of electrolyte over a, and n is a sensitivity factor having the units of reciprocal time. Beg (53) found that ethyl alcohol sensitizes copper ferrocyanide sols to precipitation by salts, whereas glycol or glycerol tends to stabilize them. Chatterji & Tewari (54) also reported the same sensitivity of a gold sol toward ethyl alcohol. The rate of the coagulation of aqueous sulfur sols by salts was followed optically by Kharin & Chaikooskaya (55), was made slower than predicted by the Smoluchowsky relation. The activation energy was found to be 2 to 3 kcal./mole. The upper limit of these coagulation concentrations, increasing with cation size, corresponded for all salts to the activity coefficient of 0.70 to 0.74, in agreement with Ostwald's rule.

More work is needed to clarify our ideas on the formation of sols from solutions. From a study of the kinetics of precipitation by electrolytes, Nielsen (56) and Lucchesi (57) concluded that the rates are dependent not only on diffusion, but also on reaction at the surfaces; as might be expected, the electrokinetic potential is of considerable importance.

Improvement over the classical method of producing metallic colloids was effected by Borel & Manus (58) who evaporated Cd, Zn, In, Na, and Li at low pressures and condensed them on a liquid surface. Particle sizes of about 1 μ were obtained at high concentrations. Chalyi & Natanson (59) formed fine iron organosols by rotating a cathode in a water-xylene interface. Sanger (60) presented a good review of the several theories pertaining to the ice-forming nucleability of substances.

Haase (61) developed general equations for sedimentation equilibrium and its relation to diffusion in nonelectrolyte dispersions, and Koelmans (62) gave an extensive review of the nature and stability of suspensions in nonaqueous media. He divided them into two groups: those in solvents with dielectric constants below and above 5, respectively. Theoretical considerations led to the conclusion that quite modest electric charges and zeta potentials are sufficient to stabilize rather coarse suspensions whereas very little

stabilization is provided by nonionized surfactants. There remains, however, incomplete agreement among investigators concerning many aspects of stability in nonaqueous dispersions.

Sediment volume with time was carefully evaluated again by Wolff (63) for suspensions in both polar and nonpolar liquids. The hyperbolic volume-time diagrams were characterized by their eccentricities, greater for polar than for nonpolar liquids, and by the decrease in half-time values with temperature and increase with surfactants. Dependence on viscosity and on the density is not clearly defined in so far as resulting volumes are concerned. An interesting method was proposed by Elton & Peace (64) for the determination of particle size distribution by measuring the sedimentation potential developed between two levels in the suspension without requiring the magnitude of the zeta potential or the specific conductivity. Ray & Deason (65) developed a multiple sheared-boundary centrifuge cell which isolates five fractions for analysis as the rotor slows down.

Continued interest in coagulation or stabilization of sols by surfactants, often promoted by technological demands, is evident from a host of publications. Running through these investigations is the theme which may be called the Overbeek mechanism (66), whereby small amounts of additive bring about coagulation by bridging between particles, and larger amounts bring about stabilization by coating each particle. Such studies include ferric oxide sols by Meguro & Kondo (67), paint systems by Arnold (68), ferric oxide, gold and arsenic sulfide sols by Tamamushi (69), and dye solutions by Meguro (70). The careful analytical work by La Mer, Smellie & Lee (71) on the coagulation of the highly complex Florida phosphate slimes also belongs in this class.

Progress has been made in developing theoretical understanding of coagulation in both streamline and turbulent flow. A kinetic equation for coagulation of coarse suspensions in streamline flow, based on the size distribution, was derived by Seregin & Figurovskii (72) and tested successfully on glass spheres in both slow and rapid coagulation. In the theory of coagulation of sols in turbulent streams, studies were reported by Levick (73) and by Frisch (74). For long coagulation times the latter's equation, as expected, reduced to Smoluchowski's relation for coagulation as a result of molecular Brownian motion, except that an eddy diffusivity constant replaces the diffusion coefficient; for rapid coagulations, the situation is more complex and this similarity breaks down.

In the important field of grinding and dispersion, Klein (75) demonstrated that the pulverizing of monodispersed sand in a ball mill can be divided into two steps, each of which can be described as a second order reaction with its own rate constant. Berry & Kameck (76) found that the periodic addition of naphthenic acid in the ball milling of ilmenite provides an adsorbed monolayer which prevents agglomeration from severely limiting particle size reduction. The grinding rate was reported to depend on two terms: one due to attrition by the balls and proportional to their surface area per unit weight

of charge, the other due to particle-particle attrition and dependent on mill diameter. For the dispersion (not grinding) of pigments in oils, the most efficient machine in reducing the last aggregates is still the roll mill. An engineering correlation of the variables and a simpler design, called a "floating" roll mill were developed by Maus *et al.* (77). Current application of the Stokes-Navier relationships to behavior in the nip between the rolls where the aggregates are broken promises to bring further advances. Moilliet (78) produced a useful review of the role of surface active agents in typical dispersion processes including mechanical disintegration, controlled precipitation, and aqueous to nonaqueous transfer. Also, Bowman & Hughes (79) presented a good review of the wetting, dispersion, and stability of titanium dioxide in a variety of liquids. It is pleasant to note that these authors criticize the use of the term "wetting" when "deflocculation" or "peptization" would serve better.

Spontaneous emulsification is emulsion formation without the aid of even slight agitation. Technically important in producing "soluble" oils, it has recently had renewed theoretical attention [Kremnev & Ravdel (80); Haydon (81); Davies & Haydon (82)]. Three conditions and any of three mechanisms may be operative: a negative interfacial tension requires the interfacial area to increase spontaneously, a positive interfacial tension in the absence of interfacial turbulence requires a diffusion of water-soluble liquid containing the oil which is left stranded as droplets, and at low positive tensions, interfacial turbulence may cause localized interfacial tension lowering with corresponding violent splitting away of drops.

Excellent reviews on the stability of emulsions and of the factors influencing phase inversion have been published by Albers (83) and by van den Tempel (84). Special mention should be made of the rate equation studies for latent coagulation made by Kharin (85). A useful review of the precipitation of aerosols by water and salt solutions has been published by Raker (86).

INTERFACES

Liquid—air interfaces.—The progress of Buff (87) and of Buff & Saltsburg (88) in developing a statistical mechanical point of view toward the surface tension properties of curved fluid interfaces is noteworthy. Following a development of a generalized Gibbs-Kelvin equation, a generalized Neumann surface tension triangle for a fluid lens showed that the classical equation must be supplemented by a thermodynamic length parameter.

Theoretical understanding of the free surface energy and surface tension of both solutions of strong electrolytes and of ionized or charged monolayers was greatly advanced. For the increase in surface tension produced by inorganic electrolytes, the distribution function approach gives agreement with experimental data up to concentrations of two molar [Schmutzer (89); Falkenhagen & Schmutzer (90); Buff & Stillinger (91); Kamienski (92)]. Davies (93) made it quite clear that the basic equation of state for surfactant films (using the notation accredited to Guastalla) $\pi_e(A - A^\circ) = kT$, where

π_c is the film pressure due to kinetic energy, can be corrected by the amount due to the cohesion between the hydrocarbon chains, π_o, and, if the film is charged, by the electrical repulsive pressure, $\Delta\pi$, which depends on the ionic concentration of the substrate and the charge density on the film. The difference between films at air-water and at oil-water interfaces can be explained on the basis of the lack of cohesive pressure in the presence of oil. Further progress in clearing up the rather chaotic published measurements on a variety of ionized and partly ionized films will no doubt be forthcoming [see also the thermodynamic treatment of Payens (94)].

It is a well known fact that boundary tension curves for soluble adsorbed films exhibit minima at some low concentration if the surfactant is impure or if inorganic salt is added. Careful examination of surface tensions versus time curves, at different concentrations of pure surfactant by Clayfield & Matthews (95) also show minima ascribed to gradual phase transitions which are temperature dependent.

Details of most of the many single component surface film studies cannot be reviewed here. Noteworthy progress is being made in measuring heats of adsorption from multitemperature isotherms and surface fugacities from equations of state [Zutranen & Ter Minassian-Saraga (96); Stauff & Rasper (97)]. Perfluoracid and amine monolayers show high repulsion in compressed films due to the large dipole of the $-CF_3$ group; these films possess the highest surface potential, $ca.$ -1000 mv., yet reported [Fox (98); Klevens & Davies (99)].

Joly (100) gave an excellent quantitative description of non-Newtonian surface viscosity in terms of a simple molecular model which includes transport of substrate molecules with the surface film, deformation of its quasi-lattice structure, and possible phase changes in the film brought on by the shear. Inokuchi (101) is reporting a series of studies of surface viscosity, and Davies (102) and de Bernard (103) described sensitive rotational viscous traction surface viscometers.

New insight into the rather unexpected heterogeneous nature of surface films and their change on compression has been revealed by electron microscopy in the hands of Ries and co-workers. Small irregular islands at low surface pressures develop discontinuous uncovered areas at intermediate pressures and become a homogeneous continuous film at high pressures. Autoradiographs of tagged molecules at low pressures showed the islands to be in the liquid expanded state surrounded by a gaseous state [Ries, Roberts & Fields (104); Ries & Kimball (105); Cook & Ries (106); Ries & Kimball (107); Ryan & Shepard (108)]. The mechanism of collapse and the magnitude of the collapse pressures are now being studied [Long, Whitmarsh & Yuan (109)]. Rate of transfer of surface films from one water surface to another through a pre-wet channel depends partly on the thickness of the underlying water layer which moves along with the film as first shown by Schulman & Teorell. Contrary to a previous report, mixed films apparently do not show any separation, but pure components in separate lenses transfer in order of

decreasing surface pressure [La Mer & Blank (110); Blank & La Mer (111)].

Studies of insoluble organic films on organic substrates are developing since Banks (112) announced his findings with a polydimethyl siloxane on several organic liquids. Ellison & Zisman (113) developed an all-teflon film balance to study films, surface active at organic-air interfaces, and included other organics such as fluorocarbons, polyfluoroquaternary ammonium compounds, organic silicates, polyacrylates and polyethers. Pertinent, too, is the effect of temperature and concentration on the activity coefficients of binary organic liquids in the bulk in comparison with those in the surface layer, possibly leading to surface demixing as examined by Teitelbaum & Osipov (114).

Many of the earlier results on retarding evaporation with surface films must be considered in doubt [for example, Bradley (115)]. Films must be under compression. Also, easily compressible films (esters) are poor retarddants compared with films which have steep surface pressure area curves (fatty acids and alcohols). The free energy barrier to evaporation increases linearly with the chain length although the principal contribution is provided by the polar, e.g., the carboxyl group [La Mer (116); Archer & La Mer (117); Rosano & La Mer (118)].

The energetics of the often specific interactions of organic monolayers on aqueous solutions with both inorganic ions, and other ionic and nonionic surfactants are rapidly being elucidated in regard to systematic variations with pH and with solution concentration. In a few cases, interactions have been studied as a function of temperature to reveal integral and isoteric heats of penetration. A few of the most pertinent references are: Durham (119); Spink & Sanders (120); Ekwall & Bruun (121); Bose & Mehrotra (122); Sobotka (123); Goodrich (124); Anderson & Pethica (125); and Bruun (126).

According to our present knowledge of free liquid films in foams, these may be divided into two types: those which arrive at an equilibrium film thickness and those whose film thickness decreases until rupture occurs. In the first case, the bubble pressure is mainly dependent on the interaction between electrical double layers, although a viscous surface film enhances stability. In the second case, the process of thinning depends on a number of possible mechanisms including surface transport and dynamic surface tension, probably involving a surface tension gradient enhanced by any local temperature gradient. Derjaguin (127) made important theoretical contributions, Mysels (128) made interesting kinematic studies of the thinning process, and Ross & Cutillas (129) reported light transmission studies of stability. Jones *et al.* (130) and de Vries (131) provided critical reviews. Various factors influencing foam formation and stability were studied by Matalon (132) using his wire frame technique. Kikuchi (133) introduced the technique of studying two-dimensional foams in the narrow space between two plates. Nevertheless, theories of foam inhibition remain in an unsettled state.

Liquid-liquid interfaces.—Among important general contributions was

that of Favstova & Vlodovets (134) who characterized the size distribution of fat spheres in milk and cream in terms of the interfacial energy and the characteristic diameter. An equation for estimating interfacial tension by Girifalco & Good (135) relates the free energies of cohesion of the separate phases to the free energy of adhesion between the phases. This approach appears to be a promising method for describing interactions at many interfaces.

As indicated previously, the work of Davies, Payens, and others sheds light on the state of films at both the water-air and water-oil interfaces where cohesion did not have to be considered. The work of Phillips & Rideal (136), for example, on the nature of films of quaternary ammonium halides and sodium alkyl sulfates at low compression and under the influence of dilute electrolytes revealed that about 50 per cent rather nonspecific ion-pair association occurs (less than the amount at the water-air interface), and a surface layer thickness of about 1.5 A in disagreement with larger values proposed earlier. Of importance in mass transfer and extraction are rates of adsorption studies, e.g., of an alkyl ammonium halide at the CCl_4-water interface, by Davies, Smith & Humphreys (137). Davies' conclusions agree with those of Blokker (138) who emphasized the influence of interfacial turbulence.

Polymer molecules spread as monolayers at oil-water interfaces reveal much about their shape, configuration, and dimensions. [These studies aid in the understanding of even more complex protein monolayers such as discussed in the section "Biological Colloids," Frisch & Simha (139); Cockbain, Day & McMullen (140).] A valuable equilibrium study is that by Smith (141) on interfacial chelation which depends on the distribution ratio of the metal ion between the two liquid phases, and on the chelation equilibrium constants.

The emulsion type is often related to the preferential solubility of the surfactant in one of the phases, according to the old Bancroft rule, but quantitative progress was recently made by Davies (142) in assigning empirical numbers to different chemical groups so that the position on an HLB (hydrophilic-lipophilic balance) scale of a given emulsifier can be estimated; apparently the logarithm of the rates of coalescence and the HLB values are directly related. Study of the elastic and viscous properties of oil-water emulsions showed that the emulsifier film sometimes has an important effect and, if the film is elastic, the emulsion can behave like a suspension of solid particles [Criddle & Meader (143); Oldroyd (144)].

Solid-liquid interfaces.—For investigations of weakly interacting solid-liquid systems, methods depending on contact angle measurements, the wetting balance, and heats of immersion continue in the forefront. Because of the ease of obtaining contact angles of sessile drops, these are widely used to predict important technological properties. Nevertheless, there is often a lack of sensitivity to small changes in surface impurities [see Chessick, Healey & Zettlemoyer (145)], or even large changes in surface concentrations

of films on solids [Bartell & Ruch (146)]. The problem created by surface roughness was reviewed critically, and the effect of the radius of curvature of the drop was considered thermodynamically by Pethica & Pethica (147). The spreading coefficient which is $F_{SV} - F_{SL} - F_L$ or γ_L ($\cos \theta - 1$) can be determined according to Padday (148) by a single measurement of the height of the sessile drop.

Zisman (149) has found that the contact angle method has been particularly fruitful in investigating the relationship of wetting and spreading to the chemical constitution of the liquid. Hare & Zisman (150) reported a class of organic liquids which are autophobic; that is, they do not spread on their own films, as O'Connor & Sanders (151) found for cationic surfactants over a narrow concentration range. Shafrin & Zisman (152) found that the wettability by water and organics of terminally fluorinated octadecyl derivatives is greater than that of perfluorinated compounds. For monolayer films of a homologous series of paraffin derivatives, Levine & Zisman (153) found the asymptotic maximum in the contact angle of methylene iodide, and the asymptotic minimum in the kinetic coefficient of friction, as a function of the paraffin chain length. The two values coincide at a chain length of 14 carbon atoms; here transition occurs from liquid condensed to solid adsorbed films. Halogenation of the chains increased cohesion and decreased the coefficient of friction. Clayfield *et al.* (154) described a method to obtain true spreading pressures and the energy of adhesion.

According to Guastalla (155), an easily operated "wetting tensiometer" measures simultaneously the surface tension of a liquid and the energy of dewetting. Of particular importance is the elucidation of the wetting-dewetting hysteresis phenomenon and the evidence that the adhesion tension approaches the surface tension for the more efficient wetting agents.

With the development of sensitive thermister calorimeters there has been a renewed interest in heats of immersion of powdered solids in liquids. One such study is the interactions of solids with a series of simple organic molecules having one polar group. This allows the polarity of the solid to be estimated from the slope of the plot of the heat of immersion vs. the dipole moment [Chessick *et al.* (156); Il'in, Kiselev & Aleksandrova (157); Zettlemoyer (158)]. According to Zettlemoyer, Young & Chessick (159), the topography of the active sites of an absorbate can be mapped by measuring the heats of immersion of the solid in a liquid after increasing amounts of the vapor of the liquid have been adsorbed. The free energies of immersion of graphites and silicas into various liquids were obtained by Craig, Van Voorhis & Bartell (160) on compressed solid plugs by integrating the Gibbs equation over the complete isotherms. With the plugs, a definitive endpoint to the isotherms at high relative pressures was obtained. Combination of such values with heats of immersion will allow entropy changes to be determined.

Heats of immersion measurements promise to be a valuable tool to study interfacial structure in the complex problem of adsorption from binary solu-

tions where only surface excesses can be followed. In the rather ideal case of butanol and water in contact with a graphitic surface, Young, Chessick & Healey (161) made considerable progress in correlating adsorption and heat of immersion data. On the other hand, Graham & Hansen (162) from a straightforward analysis of the isotherms determined the nature of the alcohol films formed on graphite from aqueous solutions. Zettlemoyer, Schneider & Skewis (163) found that the heat of immersion of a graphitic powder into surfactant solutions provides a direct method of measuring their wetting efficiency. However, the important problem is to find a satisfactory method to construct the individual isotherms for both components from the measured composite isotherm. Quite often composite isotherms show an inversion which cannot be explained by simple models, but considerable advance was made by assuming that the concentration difference is confined to the first layer at the solid surface. Thus, several calculated individual isotherms were shown to agree with vapor adsorption isotherms where adsorption of both components can be followed. Preferential adsorption can often be explained from the polarities of the solid and the adsorbates. Kipling is adding to our knowledge of the effect of surface structure [Hansen & Hansen (164); Hansen & Mai (165); Kipling (166); Blackburn & Kipling (167); Kipling & Peakall (168); Dintenfass (169)].

An understanding of the orientation of organic molecules at liquid-solid interfaces is coming from adsorption measurements at the mercury-aqueous solution interface, and from the development of differential capacitance determinations at the dropping mercury electrode [Grahame (170); Watanabe, Tsuji & Ueda (17)]. The orientation of adsorbed phases is also being determined from the dependence of the differential capacitance on the kinetics of rapid adsorption [Berzins & Delahay (172)] and the polarization of adsorbed layers [Hansen, Minturn & Hickson (173)]. The latter authors in a study of the effect of functional groups on the adsorption of pentane derivatives were able to show that these groups were oriented toward the aqueous phase; the extent of adsorption correlated with the optical polarizability of the adsorbates. Other studies in this field have recently been summarized by Frumkin (174) and Breyer (175).

In boundary lubrication, besides Zisman's work, mention should be made of Deacon & Tabor's study (176) of perfluorinated fatty acids which with reactive metals give the replenishing action needed up to temperatures somewhat greater than 250°C. This action during sliding plus low shear strength and resistance to penetration normal to the surface remain the criteria of good boundary lubricants [Bowden & Menter (177)]. Pertinent here is Derjaguin & Karassev's study (178) of the velocity profiles of liquid films on solids. Molecular orientation of polar molecules in oils is claimed, with sharp transitions indicating a boundary phase. This conclusion is not in accord with the monolayer adsorption hypothesis of Kipling or with somewhat less sensitive boundary layer viscosity studies of many other workers, nor have these workers taken surface roughness into account as suggested

by Bikerman (179). Smith & McGill (180) concluded that the decrease, upon aging, of the adsorption of fatty acids on freshly machined metals under cyclohexane to form soaps is connected with the decrease in the Kramer effect (electron emission from fresh metal surface at ordinary temperatures). It seems doubtful that these low area metal surfaces can be kept completely free of air and water in the systems employed.

Two interesting and valuable reviews on adhesion were provided by De Bruyne (181) and by Houwink (182). Of many new studies on adhesion the following two are singled out. Using model systems based on predeposited monolayers, Patrick, Doede & Vaughn (183) obtained rupture stress values by ultracentrifuging to dislodge polymers from metal substrates and then studied with an ellipsometer the thickness of the adhesive layer retained; in no case was the entire monolayer removed. Beginning in 1948, Derjaguin and co-workers demonstrated that fast electron emission occurred when polymers are rapidly stripped from substrates under high vacuum in cases where the surface of rupture does not run entirely through the polymer. Derjaguin et al. (184) reported agreement in order of magnitude between the experimental work of stripping and that calculated from the measured energy of the electrons. It appears that polymer-polymer adhesion has a dual nature: viz. chain interlacing where this can occur, coupled with a specific contribution from the electric double layer.

Of many studies bearing on flotation, the mechanism of Rogers & Schulman (185) deserves attention. If the heat of hydration of the ions is less than the lattice energy, then there is no adsorption of the surfactant and no flotation takes place; otherwise, adsorption and flotation can occur.

Numerous studies of corrosion inhibition by adsorbed films have been enhanced by Nasini & Ostacoli (186), who extended their earlier concept that layers of polar molecules on metals could be treated as membranes to ion-exchange resins. Interesting adsorption inhibition studies were also reported by Bordeau & Hackerman (187) and by Hoar (188).

Solid-gas interfaces.—The difference between the heats of solution of a solid of low and high surface area, respectively, is used by Benson and by Brunauer to determine surface energy. The best values for surface energy, measured in ergs/cm.^{2}, are: sodium chloride 276, calcium oxide 1310, calcium hydroxide 1180, siloxane silica surface 259, and silanol silica surface 129. It appears significant that the surface energy of oxides and hydroxides is substantially equal [Benson & Benson (189); Brunauer, Kantro & Weiss (190); Brunauer (191)]. The surface energies of alkali halide crystals have recently been computed by van Zeggeren & Benson (192). The surface tension of solids, whose liquids wet steel and glass, is determined in a unique manner by Sill & Skapski (193). The liquid is cast into a wedge between steel or glass plates and the melting points of the thinnest section of the wedge and of the bulk material determined. From such data the surface energies of stearic acid and of myristic acid were determined to be 179 and 116 ergs/cm.^{2}, respectively.

A more precise calculation than heretofore available, made by Benson, Channen & McIntosh (194), led to the conclusion that the orientation polarization of a polar molecule above the (100) face of a NaCl lattice is much less than expected from previous theoretical and experimental estimates.

Much effort has been devoted to studies of graphitized carbon surfaces because of their surface homogeneity and their large surface area. The homogeneity of graphitized P-33 carbon black was evident from the heats of adsorption of He and Ne determined by Greyson & Aston (195), and from the stepwise isotherms obtained by Prenzlon & Halsey (196). Graham (197) concluded that only about 0.1 per cent of the surface of this carbon was strongly heterogeneous to nitrogen adsorption compared to a value of 1.25 per cent for a proprietary carbon called Graphon. Calculations of interaction energies and vibrational frequencies for rare gases on graphite were made by Angul & Kiselev (198) and by Crowell (199). Haul & Swart (200) reported stepwise adsorption of Kr on homogeneous iron crystals.

A completely valid quantitative estimate of the site energy distribution for heterogeneous solid is unlikely soon. Nevertheless, numerous contributions concerning the characterization of adsorption isotherms, and in turn the heterogeneous nature of solid surfaces, continue to be made . Olivier & Ross (201) divided the experimental heat of adsorption into two components: one measured lateral interactions and the other interaction between adsorbate and adsorbent. The latter provides an indication of the strength of interaction as well as of the surface heterogeneity. Graham (202) applied his equilibrium function to two-dimensional condensation where it remained constant with increasing coverage and to patch formation where it increased. An isothermal equation for multilayer adsorption was derived by Joy (203) based partly on the dual-surface model of Walker & Zettlemoyer. Steele (204) developed a simple method to obtain an approximate site energy distribution function from isosteric heat and adsorption data which was applied to the experimental results by Steele & Aston (205). The method ignores lateral interactions and is complementary to that developed previously by Drain & Morrison. Peticolas (206) has made a reasonable extension of the statistical derivation of the Brunauer-Emmett-Teller (BET) equation to include an adsorbent perturbation term; this effect has often been neglected, for example, in attempting to establish the entropy of adsorbates. Takaishi & Kobayashi, A. (207) and Takaishi (208) considered entropy change due to adsorbent perturbation in the adsorption of hydrogen on metals, and suggested that the effect could be estimated from vibrational frequencies calculated from the heats of adsorption of D_2 and H_2.

To explain adsorption hysteresis, Everett and his co-workers assumed that the adsorption system comprises a large number of small domains independent of each other and capable of taking up two or more metastable states for a single value of the external variable such as pressure; conversion of one state to another is irreversible and depends on whether the variable is increased or decreased. This theory was used to explain the difference in

adsorption hysteresis for CO_2 and N_2O on porous glass and charcoal by Amberg et al. (209). Enderby (210), who also developed a domain theory (211), made an extension to include the interaction among nearest neighbors in a one-dimensional array of domains. These interactions may either aid or hinder the transformation of the neighbors. Barrer, MacKenzie & Reay (212) from an analysis of the filling and emptying of rigid pores of various shapes showed that capillary shape may be a considerable factor in developing domains which are more likely to be of the noninteracting Everett type. Quinn & McIntosh (213) showed that the domains for butane, ethyl chloride, or ammonia on Vycor glass are not independent; the stress caused by adsorption appeared to be the most important factor in dimensional change of the adsorbent.

Infrared spectrometry has been established as a potent tool for studying the adsorbed state on particulate substrates, especially by the brilliant work of Eischens. Recently, Eischens (214) reviewed progress in his aim to study the nature of the adsorbent surface, to determine the structure of chemisorbed molecules and to study adsorbed molecules while reactions are in progress. Eischens, Francis & Pliskin (215) studied the effect of coverage of CO on silica-supported Pd, Ni and Pt. The increase in the number of bands in the spectra of CO on Ni and Pd with increasing θ was interpreted on the basis of surface heterogeneity. Usually, new absorption bands indicate the advent of chemisorption, but Yates & Sheppard (216) found new ones in the physical adsorption of hydrocarbons and hydrogen on porous glass due to changes in symmetry. McDonald (217) found that nonpolar molecules caused small shifts of the surface OH band of Aerosil silica while large shifts were observed with polar molecules. Ultraviolet absorption spectrometry was applied by Robin & Trueblood (218) to the study of the adsorption of mono- and di-substituted benzene compounds on silicic acid which has the same refractive index as the cyclohexane solvent.

The nature of a variety of bonds formed in chemisorption is being resolved by others. Higuchi, Ree & Eyring (219) calculated the bond character and heat of desorption of various mono- and di-atomic molecules on metal surfaces. They concluded that on a tungsten substrate Cs and Na form pure ionic bonds and Ba and Sr form ionic bonds with some covalent character; H_2, O_2, N_2 and CO form predominantly covalent bonds with many metals. Energy and state functions for bonding electrons in localized and nonlocalized chemisorption were calculated by Kontecky (220). Photoelectric emission and conductivity measurements by Broeder et al. (221) for transition metals containing adsorbed hydrogen support the contention that the H-metal complex is essentially covalent. Culver, Pritchard & Tompkins (222) measured the surface potential differences when H_2 or CO were adsorbed on Cu, Ag, Au, Ni and Co at $-183°$, and concluded that the nature of the covalent bonds changes with amount adsorbed due to rehybridization of surface orbitals of the metals and atomic orbitals of the adsorbate.

Nuclear magnetic resonance relaxation time measurements of water adsorbed on silica gel, by Zimmerman, Holmes & Lasater (223), and by

Zimmerman & Brittin (224), revealed evidence for the coexistence of two adsorbed phases. Graham & Phillips (225) measured the shift of proton paramagnetic resonance frequency of alcohol and hydrocarbons on carbon surfaces and suggested that the surface affects the adsorbed molecules to a distance cf 25 to 30 A. Derjaguin & Zorin (226), using an elliptical polarization method for film thickness, concluded that polar bulk phases formed from vapor on glass start as discrete droplets coexisting with the adsorbed phase whereas there is no discontinuity for the nonpolar adsorbates. Gomer, Worthman, & Lundy (227), by cooling the field emission tube to liquid hydrogen or helium temperatures, where the sticking factor is nearly unity, showed that the spreading of the adsorbed film can be observed directly. In an extension of the earlier study of the mobility and desorption of oxygen on tungsten, hydrogen molecules on tungsten (on top of chemisorbed hydrogen) were found to be mobile at $20°K.$; the chemisorbed layer began to spread at $180°K.$ However, no boundary migration was observed for similar studies on nickel; this was attributed to the more uniform surface of nickel compared to tungsten. Suhrmann & Wedler (228) measured the change in resistance of deposited, translucent Ni films developed on adsorption of H_2O or CO_2. A time lag in resistance change was attributed to the time necessary for physically adsorbed molecules to move to sites active in chemisorption.

Vacancies in the d-band in transition metals play an important but not fully determined role in chemisorption. Greenhalgh, Hayward & Trapnell (229) found differences between calculated and observed heats of adsorption for H_2 on Cr and Mn and concluded that the half-filled d-bands of these metals require additional energy to destroy orbital symmetry. Wagener (230) studied chemisorption on evaporated metal films and reported fast initial rates of chemisorption of N_2 for elements in the center of the periodic table, but much slower rates for metals at the end; the implication is that d-band vacancies are important not only for chemisorption equilibrium but also for the rate of chemisorption. The importance of the d-bands of nickel in the chemisorption of benzene and cyclohexane was further demonstrated from magnetization-volume isotherms by Selwood (231).

Physical adsorption occurs over the chemisorbed species at $-195°C.$ for H_2 and CO on nickel films, according to Gundry & Tompkins (232), and for O_2 on nickel, cobalt and copper according to Zettlemoyer, Yu & Chessick (233). The latter found that the thin oxide film formed on bare Ni, Co and Cu at -195 to $25°C.$ was covered with a layer of chemisorbed oxygen anions. Activation of these oxide-covered surfaces at higher temperature converted these adsorbed ions into oxide and regenerated the surfaces for further rapid oxygen uptake. The degree of such regeneration was much less for Cu than for Ni and Co, attributed to a lower concentration of field-creating oxygen ions.

Solid-solid interfaces.—The effect of temperature on the adhesion of solids to each other and the relation between adhesion and friction have been clarified in Bowden's laboratory. In an elegant study of the adhesion of ice frozen directly onto clean metals, the stress required to break the bonds

increased linearly with temperature decrease in accord with the shear
strength of ice; that is, with clean metals the bonds at the interface are
stronger than those within the ice itself. Friction between ice and metals
increased linearly with temperature decrease, so that a parallelism between
friction and adhesion exists. The adhesion of ice on plastics is low and hydro-
phobic shearing occurs at the interface. The adhesion between metals, on the
other hand, depends upon welds produced between asperites under normal
loading and the extent to which these junctions are broken by the release of
elastic stresses when the load is removed. Thus, strong adhesion sets in at a
temperature 0.4 to 0.5 of the melting temperature at which temperature the
junctions become annealed. Friction and adhesion between metals correlate
well; low friction means poor adhesion and high friction can match high ad-
hesion where no elastic stress prevails. The role of organic monolayers in
reducing adhesion and friction seems less clear and one wonders how the
asperities can be effectively covered [Raraty (234); Bowden & Rowe (235);
Bowden & Tabor (236); Bowden (237)].

Because of the large amounts of energy expended in plastic and viscous
flow, the increase in free surface energy on separating solids is usually a
trivial part of the total energy involved. A striking exception is illustrated
in the work of Bailey (238) on the cleavage of mica which requires about 300
ergs/cm.^{2}; this is presumably just the increase in free surface energy involved.
On the other hand, Bradley (239) calculated that the possible contribution
of London dispersion forces between carbon particles is far lower than the
measured tensile strength of reinforced rubber; the physical concept of
rubber reinforcement by solid-solid interaction is apparently incorrect.

OPTICAL PROPERTIES

Scattering of radiation by colloids is pre-eminent among investigations
in this field due to the remarkable analytical applications. A significant ad-
vance was the development, by Chin, Sliepcevich & Tribus (240), of a
method for the determination of size distribution in polydispersions based
on the variation of intensity of forward scattered light at very small angles.
The theory, applicable to particle sizes large in comparison with the wave-
length of the incident light, was evaluated using a polydispersion of glass
spheres independently calibrated.

The use of specific turbidity measurements for colloidal particle size de-
terminations was examined by Heller and his associates in a series of papers.
The critical aspect in obtaining accurate average particle diameters for
nearly monodisperse polymer lattices from specific turbidity measurements
using the Mie theory involves the exact determination of the refractive index
of the scattering spheres [Tabibian, Heller & Epel (241)]. Since the refractive
index must be independent of any effects of light scattering Heller &
Tabibian (242), Matousek & Sedlacek (243), Nakagoki & Heller (244), and
Chou & Kerker (245) each confirmed the scattering contribution predicted
by the Zimm-Dandliker equation. On this basis, a new mixture rule was
formulated to obtain the necessary refractive index values. Heller & Pangonis

(246) calculated scattering cross sections, scattering coefficients, and specific turbidities from the recently extended Mie functions, and concluded that the maximum scattering power for a given material at a given wavelength increases with decreasing particle size provided the relative refractive index increases correspondingly. Small changes in the relative refractive index of the system requires the use of interpolation [Heller (247)] or extrapolation [Sedlacek (248)] from tabulated values.

The theory of light scattering in media more dense than the usual dilute colloidal dispersions has been advanced by Goldstein & Michalik (249) who extended the theory of Debye & Bueche to include the contributions of fluctuations in anisotropy to the light scattering in inhomogeneous solids, e.g., glasses and gels, and by Chu & Churchill (250) who investigated the multiple scattering and absorption of radiation having wavelengths less than the circumference of the particles. The latter authors' solution for an obliquely incident wave on a plane parallel dispersion of finite thickness was successfully checked by Scott, Clark & Sliepcevich (251) on aqueous polymer lattices.

The influence of heterogeneous interparticle spacing on small angle x-ray scattering was evaluated theoretically by Kratky & Porod (252) for nonspherical particles, and by Hosemann & Joerchel (253) using a model to simulate polydispersed clusters of particles. The maximum in the scattering pattern anticipated from theory was not found by Kranjc (254) in a study of aluminum hydroxide at widely different packing densities. The apparent mean particle diameters increased while the relative intensity of the scattered radiation decreased at larger packing densities, probably due to association of particles during compaction. Debye, Anderson & Brumberger (255) demonstrated a very useful method of determining the specific surface of porous materials from the angular intensity distribution of x-rays scattered at small angles. Experimentally determined specific surfaces from this method are usually somewhat greater than those calculated from adsorption measurements, presumably because area inaccessible to gas molecules is examined by the x-rays.

SURFACTANT SOLUTIONS

In addition to optical properties and the properties of surfactants at interfaces, discussed heretofore, several recent advances deserve attention. The multitude of c.m.c. (critical micelle concentration) determinations and micelles in nonpolar solvents, on which little new critical work has appeared, cannot be discussed here.

The central problem concerns the exact nature of the micelles in these association colloids. That micelles usually form as spherical aggregates of about 80 to 100 units in aqueous solutions over a narrow concentration range at the c.m.c. is rather well-accepted. The large number of reports conflicting with this statement, it now seems clear, can be ascribed to changes in size and shape brought about by changing circumstances. Thus, increases either in ionic strength or in surfactant concentration above the c.m.c. increase

the micelle size somewhat. The shape tends to change, too, at least to oblate spheroid and often to elongated structures as the work, for example, of Pilpel (256) on viscosity, of Abbot & Tartar (257) on diffusion, or of Shirai & Tamamushi (258) on high frequency conductivity suggests. The chain length must also be considered, for long chains can cause deviation from spherical shape as Tartar (259) decided. The important analyses of Mysels (260) and of Prins & Hermans (261) showed that the effect of the double layer on light scattering is to make the micelle slightly larger than otherwise supposed. Because theories of micelle formation based on the opposition between chain attraction and ionic attraction lead to incorrect calculations of micelle size distribution and also because they cannot account for nonionic micelles, Reich (262) reconsidered the thermodynamics and got the necessary narrow size distribution range by focusing attention on the free energy decrease in the system rather than in the individual micelle. The statistical mechanical treatment of Hoeve & Benson (263) also gave the proper narrow size distribution; they decided that the chains are not curled up in the center (as Reich had also found) and that plate-like rather than rod-like structures develop at high concentrations. Ooshika & Ikeda (264), somewhat similarly, and almost simultaneously to Reich, calculated the free energy per ionic micelle particle in terms of adsorption equilibrium of the counterions; agreement with the double layer theory approach may be quite special because this theory also cannot account for nonionic micelles. Overbeek & Stigter (265) showed that high surface potentials of the Hoskin type were required to treat the electrical part of the free energy of micelle formation; the nonelectrical part was about $1\ kT$ per carbon in the chain and independent of chain length. These workers together with Stigter & Mysels (266) concluded that the curvature of the double layer makes them far from ideal even at the c.m.c.; the latter suggested that a "surface roughness" of the micelle would have to be considered to account for discrepancies between measured and calculated zeta potentials. Most of this work was done with micelles of sodium lauryl sulfate which Stigter, Williams & Mysels (267) claim on the basis of diffusion studies carry about a monolayer of adsorbed water. A remaining and puzzling conclusion of a number of investigators including Mysels & Dulin (268), who used tracer electrophoresis, is that ionization of the micelles seems to increase slowly as concentration is increased.

Another problem is provoked by the sharp breaks in integral heats of solution curves at the c.m.c. [Hutchinson & Winslow (269); Zettlemoyer, Schneider & Skewis (270); Goddard & Benson (271)]. Perhaps further more careful work will eliminate the breaks and give only a change in slope at the c.m.c. (more plausible thermodynamically) as reported for C_8 and C_{10} sulfates by the last workers.

Although Hutchison, Inaba & Baley (272) believe solubilization is subject to the normal laws of physical chemistry and Hutchison & Mosher (273) found only a small abnormality in the partial molal volume of alcohols in sulfates (suggesting a hydrocarbon center structure just slightly looser than in liquid hydrocarbons), there is much evidence that special phenomena are

involved. Viscosity measurements on both anionic and cationic surfactant solutions containing increasing amounts of organics show changes to elongated micelles, sometimes even of several types [Markina, Pospelova & Rehbinder (274); Bose & Mehrotra (275); Smith & Alexander (276)]. Also, solubilization in considerable amounts can occur well below the c.m.c. [Ekwall (277)] as emphasized by the term "comicellization" [Valko & Epstein (278)]. Finally, from the spectra of solubilized dyes, Sasaki, Okuyama & Saito (279) conclude that micelles contain some internal water molecules; however, the water molecules might follow the dyes.

BIOLOGICAL COLLOIDS

Tremendous headway is being made in the application of colloid and surface chemistry techniques in the life sciences. Space will only permit attention to a few developments.

On the theoretical side, Dray & Sollner's confirmation (280) of their theory of dynamic polyionic potentials across membranes, and Hill's elegant extension to proteins of his localized unimolecular gas adsorption theory for sites of different energies are outstanding. Scatchard, Coleman & Shen (281) developed a cell to measure changes in emf. with change in concentration or composition between ion exchange membranes and protein molecules, and Mach (282) used a membrane cell to distinguish between alkaloid solutions.

Electrophoresis has been used successfully to determine complexing between proteins [Jameson & Barnet (283); Baker and co-workers (284)] and the effect of conditions on size and shape [Wagner & Scheraga (285); Aoki & Foster (286)]. The albumin-globulin complex in undiluted serum and antigen-antibody complexes were revealed by the boundary movements. The earlier suggestion of both Scatchard and Tanford that serum albumin is expanded below pH 3.5 was substantiated.

An intriguing study by Riehl (287) of the temperature dependency of the conductivity of gelatin to which small amounts of water was added, revealed the same activation energy as in ice (21 kcal./mole). Therefore, proton displacement is believed responsible for energy and charge transport in both. This explanation neglects contributions of salt ions in more disperse systems. As a matter of fact, Tanford's equations (288) for the electrostatic free energy of globular protein ions show a considerable decrease in free energy if salt ions penetrate their interiors. Tests showed, however, that the equations did not fit experimental data on normally sparingly-solvated protein ions but only on expanded ions. It is interesting to compare the work of Riehl with that of Couper, Eley & Hayward (289) who showed that, while freeze-dried bacteria containing hydrogenase did not catalyze the parahydrogen conversion, a small quantity of water restored activity which reached a maximum only when water equal to three times the dry weight of bacteria was added.

Studies of proteins at solution interfaces involving Langmuir balance measurements have been intensified usually with either of two objects in mind: to study the behavior of films as models of natural cell membranes

and their interaction with biologically important substrates, or to investigate specific properties such as molecular weight or the effect of unfolding of enzymes on activity. Films produced by adsorption from solution of polyampholytes, whether proteins or model synthetic polymers, tend to change with time so that interest in the more stable spread monolayers has grown. Yet the difference cannot be discounted that spread monolayers are usually made up of flat extended molecules, whereas those formed by adsorption from solution may be three-dimensional coils. The latter was recently confirmed for serum albumin by Bateman & Adams (290) who determined by the techniques of Langmuir and Blodgett that thick, not extended, layers were deposited from solutions under various conditions on to barium stearate films. Thus, when Eley & Hedge (291) using the Schulman-Rideal technique of injecting a dissolved protein under a previously spread protein found no specific interaction between fibrinogen and thrombin (which of course occurs in the clotting reaction), the critical spacing may have been lost on spreading. On the other hand, at decane-water solution interfaces, Cockbain (292) reported serum albumin at pH 5.6 is adsorbed as an extended monolayer, although his technique depended upon repeatedly preparing emulsions of the same interfacial area. By studying changes in surface pressure or injecting various quantities of proteins under lipide films as model membranes, Eley & Hedge (293) showed from discontinuities in the isotherms that the first adsorbed layer of protein is unfolded and the second remains globular. From studies at several temperatures, these workers were able to investigate the thermodynamics of film penetration by proteins; they concluded that slightly less than half of the available side chains penetrate stearic acid films and far less penetrate cholesterol films. A quite different and unique method of studying interaction between stearic acid and serum albumin developed by Sher & Sobotka (294) is to follow the removal of Blodgett films of the lipide on metal slides by solutions of the protein under various conditions of temperature, pH, etc. Sobotka, Santamaria & Demeny (295) studied urea denaturated albumin in the same way. Therefore, there is a diversity between the groups involved in the two adsorptions. Saunders (296) produced stable films of natural lecithins at the boundary between such aqueous phosphatide sols and aqueous electrolyte solutions as model cell membranes. Miller & Katchalsky (297) examined the surface properties of adsorbed time-stable films of synthetic polyampholytes (methacrylic acid and 2-vinyl-pyridine) to resemble some of the properties of proteins.

Spread trypsin films at low surface pressure on water solutions gave no recoverable activity for Ray & Augenstine (298), and lost activity with age even at higher surface concentrations. Activity is also lost at negatively charged lipide-stabilized oil/water interfaces as reported by Fraser & Schulman (299), in proportion to the strength of adsorption which is greatest between sulfonate and phosphate interfaces and the $-NH_3^+$ groups on the trypsin (the active center, the imidazole group, is apparently not involved).

These recent advances in the colloid and surface chemistry aspects of proteins and model cell membranes indicate that in particular the nature and

distribution of their active sites are unfolding. Whether the exterior wall of cell membranes is predominantly peptide, lipide or polysaccharide remains a moot point. Correlation of lecithin sol properties with those of red blood cell membranes led Elworthy & Saunders (300) to conclude that the cell membrane surface has a lipoid nature. James (301) decided that the normal cells of *Aerobacter aerogenes* have a characteristic polysaccharide surface in contrast to a lipide surface produced in the presence of crystal violet. In so far as bactericidal action of antibiotics or ionic surfactants is concerned, however, the exciting work of Few (302) and of Gilby & Few (303) focussed attention on the protoplast membrane under the cell wall as the seat of the action. The same order of active groups on a surfactant, $-NH_3^+ > -N(CH_3)_3^+ > -SO_4^- > SO_3^-$, was found for killing the normal bacteria as for lysis of the protoplasts. Phospholipide content in the protoplast, demonstrated by infrared spectra, can account for the more favorable cationic adsorption indicated by this series. A similar conclusion was reached for decapeptide antibiotics since the more basic ones interact more strongly with the Gram negative organisms having a high content of lipide phosphate groups and the less basic ones with the Gram positive bacteria having a low content.

The likely possibility that the primary stimulus in the sense of smell is sorptive in character was supported by the studies of Moncrieff (304) on the selective concentration of odorous substances achieved by freshly-killed sheep heads. An important contribution by Davies & Taylor (305) defined the olfactory threshold (molecules/cc.) quantitatively in terms of the adsorption energy in passing from air to lipide-aqueous surfaces of the olfactory membrane and of the sizes and shapes of the odorant molecules. The number of molecules p required to be adsorbed on a site is calculated from the molecular cross-sectional area $A[1/p = 0.02A - 0.162]$. The adsorption energy is obtained from vapor pressure and interfacial tension measurements. From p and the adsorption energy, the olfactory threshold is readily calculated. It appears that the sense of smell is rapidly being reduced to scientific principles, although questions of intensity and type of odor remain unresolved.

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